

CANADIAN THESES ON MICROFICHE

THÈSES CANADIENNES SUR MICROFICHE



National Library of Canada
Collections Development Branch

Canadian Theses on
Microfiche Service

Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada
Direction du développement des collections

Service des thèses canadiennes
sur microfiche

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

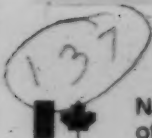
La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

**THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED**

**LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE**



National Library
of Canada

Bibliothèque nationale
du Canada

0-315-01331-0

Canadian Theses Division

Division des thèses canadiennes

Ottawa, Canada
K1A 0N4

PERMISSION TO MICROFILM — AUTORISATION DE MICROFILMER

• Please print or type — Écrire en lettres moulées ou dactylographier

Full Name of Author — Nom complet de l'auteur

ISOBEL JULIA BROWN

Date of Birth — Date de naissance

31 AUGUST 1961

Country of Birth — Lieu de naissance

UNITED KINGDOM

Permanent Address — Résidence fixe

THE RETREAT
CUDHAM LANE SOUTH
CUDHAM, SEVENOAKS, KENT
TN14 7QB
ENGLAND

Title of Thesis — Titre de la thèse

GOLD-BISMUTH-COPPER SKARN MINERALIZATION IN THE
MARN SKARN, YUKON

University — Université

U. OF ALBERTA

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée

MASTERS

Year this degree conferred — Année d'obtention de ce grade

1985

Name of Supervisor — Nom du directeur de thèse

B. E. NESBITT

Permission is hereby granted to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

L'autorisation est, par la présente, accordée à la BIBLIOTHÈQUE NATIONALE DU CANADA de microfilmer cette thèse et de prêter ou de vendre des exemplaires du film.

L'auteur se réserve les autres droits de publication; ni la thèse ni de longs extraits de celle-ci ne doivent être imprimés ou autrement reproduits sans l'autorisation écrite de l'auteur.

Date

14 December 1984

Signature

I J Brown

THE UNIVERSITY OF ALBERTA

GOLD-BISMUTH-COPPER SKARN MINERALIZATION IN THE MARN SKARN, YUKON.

by



Isobel J Brown

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF Master of Science

GEOLOGY

EDMONTON, ALBERTA

SPRING, 1985

THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR Isobel J Brown
TITLE OF THESIS GOLD-BISMUTH-COPPER SKARN MINERALIZATION IN THE
MARN SKARN, YUKON.

DEGREE FOR WHICH THESIS WAS PRESENTED Master of Science
YEAR THIS DEGREE GRANTED SPRING, 1985

Permission is hereby granted to THE UNIVERSITY OF ALBERTA LIBRARY to
reproduce single copies of this thesis and to lend or sell such copies for private,
scholarly or scientific research purposes only.

The author reserves other publication rights, and neither the thesis nor
extensive extracts from it may be printed or otherwise reproduced without the
author's written permission.

(SIGNED) I Brown

PERMANENT ADDRESS:

The Retreat
Cudham Lane South
Cudham, Near Sevenoaks
Kent, TN14 7QB
England

DATED 14 December 1984

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled
GOLD-BISMUTH-COPPER SKARN MINERALIZATION IN THE MARN SKARN, YUKON,
submitted by Isobel J Brown in partial fulfilment of the requirements for the degree of
Master of Science.

Bruce Nestor

Supervisor

Philippe Estévez

Gh. Cumming

Date *14 December 1984*

A. Bardsley

ABSTRACT

The MARN claims are located on the western margin of the Middle Cretaceous Mount Brenner Stock, which forms part of the Tombstone range of the Ogilvie Mountains in the Yukon Territory. Low-grade gold-copper bismuth mineralization occurs in two skarn bodies on the northern and southern contacts of a tongue-like projection of the Mount Brenner Stock. Only the northernmost of these two skarns contains significant and potentially economic grades of gold. The contrast in metal grades between the two skarns is a result of differences in the skarn development from the earliest period of prograde skarn at temperatures in excess of 600°C, through a later mineralization stage, until a final period of limonitic alteration.

In the northern area, a complex configuration of impermeable quartz-rich lithologies and monzonite sills produced an inhomogeneous and unpredictable skarn development. In contrast, the more simple geology of the southern area produced a massive and consistent skarn horizon. The degree of permeability of the pyroxene skarn appears to have controlled the volume of retrograde alteration and mineralization. The lower metal grades in the southern skarn reflects the more restricted permeability of this unit compared to the skarn in the north. The mineralogy of both skarns is dominated by iron-rich pyroxenes of the diopside-hedenbergite series. The compositions range from Hd_{10-20} in the northern skarn to Hd_{80-100} in the south.

The style of mineralization is similar in the two skarns. Pyrrhotite and chalcopyrite were deposited from fluids between 300°C and 500°C by the replacement of earlier skarn silicates. Bismuth and gold-bearing minerals, including hedleyite ($Bi_{14}Te_3$), native bismuth and electrum, formed below 300°C as veinlets and blebs closely associated with the more voluminous sulphides.

Intense limonitic alteration characterizes the northern skarn and is poorly developed in the southern area. Secondary enrichment or upgrading of the skarn might have occurred during this stage.

The prograde assemblages of the iron-rich and mineralized skarns are represented by $\log fO_2$ - $\log fS_2$ diagrams and define a reduced skarn environment similar to those determined for reduced tungsten skarns of Japan.

The conditions of mineralization are not well constrained; however the sulphide mineralogy suggests $\log fS_2 = -8$ to -10 . the absence of magnetite places a maximum fO_2 on the mineralizing fluids.

It is concluded that the contrast in metal grades between the two skarns resulted from processes initiated soon after contact metamorphism. It appears to be unlikely that any significant gold or copper values might be found in as yet unsampled skarn from the southern area.

ACKNOWLEDGMENTS

This thesis was carried out under the invaluable guidance and supervision of Bruce Nesbitt. Financial support for field work was provided by Noranda Exploration Ltd. I am very grateful to John Biczok of Noranda who gave advice and assistance in the field and who provided innumerable maps, reports and sections.

I am greatly indebted to Steve Launspach for his assistance with the microprobe analyses and for his continued patience and enthusiasm.

The manuscript benefitted from critical reading by B. Nesbitt, P. Erdmer and H. Badsgaard to whom I am grateful.

Frank Dimitrov provided advise on draughting and photography.

Finally, I would like to express my deep gratitude to Amarendra Changakoti and Kevin Ansdell for their support and encouragement throughout the course of this project.

Table of Contents

Chapter	Page
1. INTRODUCTION	1
1.1 REGIONAL GEOLOGY	1
2. SKARNS	5
2.0.1 INTRODUCTION AND CLASSIFICATION	5
2.0.2 SKARN EVOLUTION AND ZONING	6
2.0.3 MINERAL EQUILIBRIA AND SKARN FACIES	7
2.0.4 GOLD-BEARING SKARNS	9
3. THE GEOLOGY OF THE MARN CLAIMS	14
3.1 INTRODUCTION	14
3.1.1 THE DEVONO-MISSISSIPPIAN FORMATION (DMSc)	14
3.1.2 TAHKANDIT LIMESTONE	16
3.1.3 JURASSIC SCHIST	16
3.1.4 INTRUSIVES	17
3.1.5 STRUCTURE	22
3.2 THE GEOLOGY OF THE MINI-GRID AREA	22
3.3 THE GEOLOGY OF MINERAL GULLY	30
3.4 CONDITIONS OF CONTACT METAMORPHISM	36
4. PETROLOGY AND PARAGENESIS OF THE SKARNS	39
4.1 INTRODUCTION	39
4.1.1 ANALYTICAL TECHNIQUES	39
4.2 STAGES OF SKARN DEVELOPMENT	40
4.2.1 CONTACT METAMORPHISM	40
4.2.2 BARREN WOLLASTONITE-BEARING SKARN	40
4.2.3 IRON-RICH, PYROXENE SKARN	54
4.2.4 MINERALIZATION	63
4.2.5 LATE ALTERATION	73
4.3 SUMMARY AND PARAGENESIS	82
4.4 LITHOLOGICAL CONTROLS ON SKARN FORMATION	86
4.5 GOLD MINERALIZATION AND METAL GRADES	87

5. CONDITIONS OF SKARN FORMATION AND MINERALIZATION	90
5.1 INTRODUCTION	90
5.2 THE EARLY SKARN STAGE	90
5.2.1 IRON CONTENT OF THE SKARNS	90
5.2.2 FLUID COMPOSITION	95
5.2.3 RETROGRADE ALTERATION	98
5.2.4 THE SIGNIFICANCE OF EARLY SKARN FOR LATER MINERALIZATION	98
5.3 MINERALIZATION	99
5.3.1 ENVIRONMENT OF DEPOSITION	99
5.3.2 METAL TRANSPORT AND DEPOSITION	102
5.4 LATE OXIDATION AND ALTERATION	103
5.5 COMPARISON OF THE MARN WITH OTHER SKARN TYPES	105
5.6 SUMMARY AND CONCLUSIONS	105
REFERENCES	109
APPENDIX 1. COMPLETE ELECTRON MICROPROBE ANALYSES OF SKARN SILICATES .	113
APPENDIX 2. REACTION CONSTANTS CALCULATED BY SUPCRT AND USED IN THE CONSTRUCTION OF FIGURES 5.4 AND 5.5	140
APPENDIX 3. REACTION CONSTANTS USED IN THE CONSTRUCTION OF FIGURE 5.7 ..	142

LIST OF TABLES

2.1. Characteristics of the major skarn types.....	10.
4.1. Analyses of joseite and hedleyite	80.
4.2. Electron analyses.....	81.

LIST OF FIGURES

1.1 Location of the MARN claims.....	2.
1.2 Geological map of the Tombstone area.....	3.
3.1 The geology of Mineral Gully and Mini-Grid.....	15.
3.2 Compositions of augites from the monzonite sill	20.
3.3 Location of sampled drill holes and exposures	23.
3.4 Section A through the Mini-Grid skarn	25.
3.5 Section B through the Mini-Grid skarn.....	26.
3.6 Section C through the Mini-Grid skarn.....	27.
3.7 Section D through the Mini-Grid skarn	28.
3.8 East-West section through Mini-Grid	29.
3.9 Section through Mineral Gully skarn.....	32.
3.10 Longitudinal section of Mineral Gully.....	33.
3.11 P-T conditions of contact metamorphism.....	38.
4.1 Location of the main skarn types.....	41.
4.2 Contact zone between monzonite and barren skarn.....	45.
4.3 Variation in Al and Fe content of skarn pyroxenes.....	46.
4.4 Paragenesis of skarn from DDH-27.....	47.
4.5a Paragenesis of skarn from DDH-37	53.
4.5b Paragenesis of anorthite-wollastonite skarn, Mineral Gully.....	53.
4.6 Paragenesis of iron-rich skarn, Mini-Grid	57.
4.7 Paragenesis of hedenbergite skarn, Mineral Gully	58.
4.8 Composition of skarn pyroxenes	83.
5.1 Simplified paragenesis of the skarn types	91.
5.2 Compositional variation between pyroxenes of different skarn types	92.
5.3 T-XCO ₂ diagram of relevant equilibria	93.
5.4 LogfO ₂ -LogfCO ₂ diagram at 500°C and 2Kbars for Ca-Fe-Si-C-O system	96.
5.5 LogfO ₂ -LogfCO ₂ diagram at 600°C and 2Kbars for Ca-Fe-Si-C-O system	97.
5.6 Bi-Te system	100.
5.7 LogfS ₂ -LogfO ₂ diagram for relevant sulphide and oxide minerals at 300°C and 400°C	101.

5.8 Idealized section through the Mini-Grid skarn.....	107.
--	------

LIST OF PLATES

1a. View of the monzonite sill.....	18.
1b. View of Mineral Gully.....	18.
2a. Massive skarn in Mineral Gully	34.
2b. Skarn lens in Mineral Gully	34.
3a. Drill core from DDH-37.....	42.
3b. Drill core from DDH-27	42.
4. Replacement textures in skarn from DDH-27	48.
5a. Anorthite-wollastonite skarn, Mineral Gully	50.
5b. Garnet-rich skarn, DDH-37	50.
6a. Scheelite in hedenbergite skarn, Mineral Gully	55.
6b. Andradite-bearing float, Mineral Gully	55.
7a. Iron-rich grossular in skarn, Mineral Gully	59.
7b. Contact between skarn and monzonite.....	59.
8a. Open-space filling by calcite in skarn, Mini-Grid.....	61.
8b. Actinolite replacement of pyroxene skarn	61.
9a. Contact between wollastonite marble and skarn	64.
9b. Coexisting wollastonite and hedenbergite.....	64.
10a. Sulphide and actinolite veining in skarn	67.
10b. Replacement of pyroxene by pyrrhotite and chalcopyrite.....	67.
11a. Magnetite rimmed by pyrrhotite.....	69.
11b. Molybdenum in chalcopyrite	69.
12a. Pyrite replacing covellite	71.
12b. Electrum and bismuth minerals in chalcopyrite.....	71.
13a. Grain of electrum and bismuth minerals in chalcopyrite.....	74.
13b. Bismuthinite replacing bismuth	74.
14a. Bismuth minerals.....	76.
14b. Fracture-filling vein of electrum, bismuth and hedleyite	76.
15a. Arsenopyrite and electrum in chalcopyrite	78.
15b. Exsolution of electrum and bismuth in arsenopyrite	78.
16a. Native gold in secondary copper minerals and iron oxides	84.

16b. Limonitic alteration of monzonite and skarn	84.
--	-----

MINERAL ABBREVIATIONS AND FORMULAE

SKARN MINERALS

Q	Quartz	SiO_2
Andr	Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{11}$
Gr	Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{11}$
Di	Diopside	$\text{CaMgSi}_2\text{O}_6$
Hd	Hedenbergite	$\text{CaFeSi}_2\text{O}_6$
Sal	Salite	$\text{Ca}(\text{Fe}_{1-x}\text{Mg}_{x-1})\text{Si}_2\text{O}_6 - \text{Ca}(\text{Fe}_{1-x}\text{Mg}_{x-2})\text{Si}_2\text{O}_6$
An	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Woll	Wollastonite	CaSiO_3
Cal	Calcite	CaCO_3
Act	Actinolite	$\text{Ca}_2(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Trem	Tremolite	$\text{Ca}_2\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Id	Idocrase	$\text{Ca}_{10}(\text{Mg,Fe})_2\text{Al}_2\text{Si}_8\text{O}_{34}(\text{OH})_2$
Zo	Zoisite	$\text{Ca}_2\text{Al}_2\text{Si}_4\text{O}_{12}(\text{OH})_2$
Pr	Prehnite	$\text{Ca}_2\text{Al}_2\text{Si}_4\text{O}_{12}(\text{OH})_2$
Sch	Scheelite	CaWO_4
Mag	Magnetite	Fe_3O_4
Hem	Hematite	Fe_2O_3
Ilm	Ilmenite	FeTiO_3
Cpy	Chalcopyrite	CuFeS_2
Cb	Cubanite	CuFe_2S_4
Po	Pyrrhotite	FeS
Py	Pyrite	FeS_2
Aspy	Arsenopyrite	FeAsS
Loell	Loellingite	FeAs_2
Bn	Bornite	Cu_5FeS_4
Bi	Native bismuth	
Bism	Bismuthinite	Bi_2S_3

METAMORPHIC MINERALS.

Bt	Biotite
Gra	Graphite
Crd	Cordierite
Plag	Plagioclase feldspar
Sill	Sillimanite
And	Andalusite
Ky	Kyanite
Musc	Muscovite
Alm	Almandine
Tourm	Tourmaline

1. INTRODUCTION

The MARN claims are located in the Tombstone range of the Ogilvie Mountains, 55km north of Dawson City in the west-central Yukon (Fig. 1.1). Exploration work was first carried out at the MARN in 1978 by Mattagami Lake Mines Ltd. The claims are held at present by Noranda Exploration Ltd. An exploration and drilling program between 1978 and 1983 resulted in the delineation of two skarn bodies containing some significant gold and copper values and minor enrichment of tungsten and silver. The diamond drilling program concentrated on the northernmost of the two skarns, where the most encouraging grades of gold were found. The principal aims of this thesis were to characterize the skarn mineralogy and to identify the ore assemblages. In addition, it was hoped that some of the factors that controlled the development of the skarn and mineralization would be clarified. An assessment of the potential for higher-grade ore in the southern skarn was a major objective of this study.

Sampling over the whole area of the claims was carried out in order to assess the extent of the influence of the skarn event. A large number of electron-microprobe analyses of skarn minerals are included in this report. The chemistry of the pyroxenes in particular proved useful in comparing the lower grade southern skarn and the higher grade skarn to the north. Finally, the environment of skarn formation in terms of T, P, fO_2 , fCO_2 , and fS_2 is discussed and a brief comparison is made with other skarn types.

1.1 REGIONAL GEOLOGY

The Ogilvie Mountain range crosses the boundary of two major tectonic elements; the Selwyn Basin to the south and the Mackenzie Platform to the north (Thompson and Roots, 1982). The MARN is associated with the early Middle Cretaceous Mount Brenner Stock which intrudes the basinal sequence close to the shelf margin (Fig. 1.1). The shelf and basin assemblages are separated by the Dawson Fault, a major low-angle thrust fault, seen as the most northerly thrust in Figure 1.2. To the south, the Proterozoic to Upper Paleozoic basinal sequence terminates at the Tintina Fault.

The structural styles of the northern and southern Ogilvies are very different, reflecting the major tectonic divisions. In the Tombstone area, the structure is dominated by late Early Cretaceous thrust faulting (Figure 1.2). Imbricate zones of southeast dipping

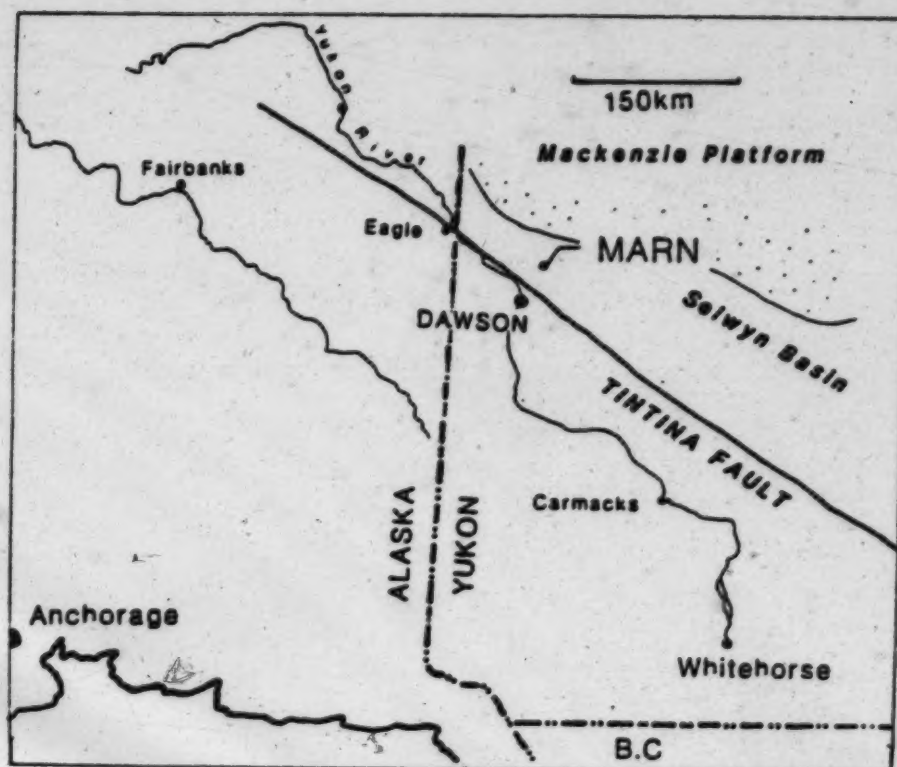


Figure 1.1. Location of the MARN claims.

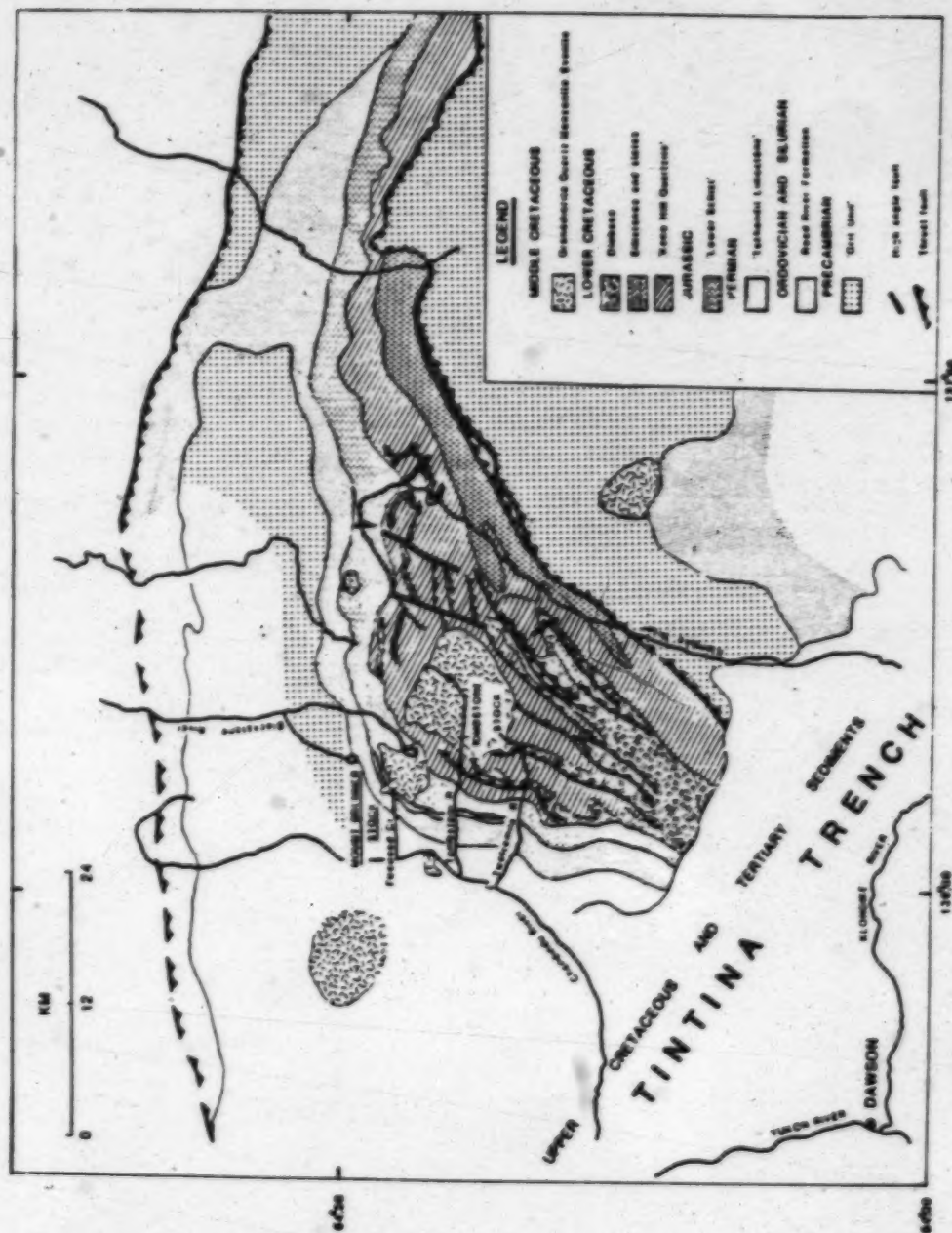


Figure 1.2. Geological map of the Tombstone area.

thrust faults in the Lower Cretaceous rocks separate deeper thrusts that affect Precambrian strata. North of the Dawson Fault where the tectonic style is very different, Upper Cretaceous rocks were involved in Laramide deformation (Tempelman-Kluit, 1970).

The Tombstone and Mount Brenner Stocks represent the northernmost limit of a chain of post-tectonic granitoids, that extend into the Selwyn Mountains of the South-Central Yukon. The intrusives have been dated at 90Ma (Tempelman-Kluit, 1970) and range from syenite to quartz-monzonite compositions.

Tempelman-Kluit (1970) divided the units of the Tombstone area into an Upper Division of Permian and younger rocks which lie unconformably on the Precambrian to Silurian-age Lower Division. Units of the Ordovician-Silurian Road River Formation are the oldest rocks in the MARN area.

2. SKARNS

2.0.1 INTRODUCTION AND CLASSIFICATION

The term 'Skarn', encompasses a wide variety of calc-silicate rock types, that formed by the metasomatic replacement of calcareous rocks at elevated temperatures. Several review papers on skarns have been published, the most comprehensive being those of Einaudi et. al. (1981), and Zharikov (1970).

Skarns may form in a variety of environments, however, the largest and most economically important are those developed in limestones adjacent to granitoid intrusions. Reaction skarns occur between dissimilar lithologies in regional or contact metamorphic environments, and form by the two-way movement of elements over short distances. These are rarely mineralized, and are economically insignificant in comparison to large systems involving substantial fluid movement over greater distances.

Carbonates are the most susceptible rock-types to replacement. Skarn formed from a carbonate protolith is termed 'exoskarn', while that developed in igneous rocks, or in hornfels, is 'endoskarn'. The degree of development of endoskarn varies considerably between skarns, being less common in deeper level environments.

Iron, silicon, magnesium, aluminum and manganese are the main elements added to the carbonate horizon to produce the characteristic skarn calc-silicate minerals. The fluids transporting these elements include components of magmatic fluids emanating from the cooling intrusive, and of circulating, heated meteoric water. The degree of the contribution from each can sometimes be determined from a study of stable isotopes. Taylor and O'Neil (1977), documented a progressive increase in the meteoric component of skarn fluid through time, in garnet-pyroxene skarns from the Osgood Mountains in Nevada.

The most useful and widely used classification of skarns is based on the major economic minerals; tungsten, iron, copper, lead-zinc, molybdenum and tin. Further subdivision is by gangue mineralogy, intrusive association and tectonic environment. A summary of the most important characteristics of each type is illustrated in Table 2.1. For more detail, the reader is referred to Einaudi et al. (1980). The classification scheme favoured by Soviet authors, and reviewed in Zharikov (1970), is the division into calcic and

magnesian skarns, formed from calcite limestones and dolomitic limestones, respectively. These are further subdivided into diffusional and infiltrational skarns, based on the mechanism of skarn formation and metasomatism. Diffusional skarns are equivalent to reaction skarns, while infiltrational skarns are the larger and often mineralized systems.

2.0.2 SKARN EVOLUTION AND ZONING

The process of metasomatism involves the change in the composition of rocks by the mass transfer of materials, in contrast to the isochemical recrystallization during contact metamorphism. Diffusion metasomatism is the process by which species migrate through a stagnant pore fluid, in response to a chemical potential gradient. Infiltration involves the flow of fluids through intergranular pore-spaces or fractures in response to a thermal or pressure gradient. Infiltration requires a degree of permeability and porosity that may not be present at high pressures. Consequently, diffusion becomes the more important mechanism at higher pressures.

The end result of metasomatism is to equalize chemical potential gradients, forming rocks of similar chemistry. If the metasomatic process does not go to completion, a series of metasomatic zones will result. The effects of diffusion and infiltration metasomatism are distinguished by compositional changes within and between zones (Korzhinskii, 1970; Burt, 1974; Fletcher and Hofmann, 1974). Infiltration metasomatism results in low compositional variations of solid solution minerals within zones, but sharp compositional changes across zonal boundaries. Mineral assemblages of adjacent zones are not in equilibrium and frequently inner zones, produced by later increments of fluid, replace outer zones. In contrast, diffusion metasomatism results in a continuous compositional change in solid solution minerals, although mineral assemblages may show sharp zonal patterns. The limited compositional variations of pyroxenes and garnets within each zone of many large skarn deposits is unmistakably the signature of infiltration metasomatism. Slight compositional variations within zones may represent an intermediate position between the two mechanisms, or incomplete equilibrium between the fluid and minerals.

Systematic changes in the chemistry of mineral assemblages are characteristically produced by the skarn-forming processes. Mineralogical and chemical zoning is

recognised in almost all skarns, forming a consistent pattern within any single deposit. A sequence of zones at the Strawberry mine in California illustrates the progressive depletion of calcium marbles to the granodiorite (Nockleberg, 1981). The sequence of zones, which from marble to intrusive are; wollastonite, garnet, pyroxene, and hornblende skarns, show discontinuities in their bulk chemistry attributed to infiltration metasomatism. Successive increments of fluid from a single source, reacting with earlier skarn zones, and unaltered marble may explain the zoning pattern and the replacement of outer zones by inner zone assemblages.

A phase of retrograde alteration, corresponding to the final meteoric stage of Taylor and O'Neil (1977), is often superimposed over the early zoning pattern. Garnet and pyroxene are replaced by assemblages including actinolite, tremolite, calcite, quartz, biotite and iron oxides. The intensity of alteration of the early silicates by lower temperature fluids depends on the permeability of the rocks and the intensity of the fluid circulation. Skarns associated with high level, porphyry copper systems, such as at Bingham, Utah, are typically intensely altered by late hydrothermal fluids, in contrast to slightly altered copper skarns associated with barren stocks, and more deeply emplaced tungsten skarns. With the exception of scheelite, the main phase of ore deposition occurs during this retrograde stage. Mineralization often coincides with a particular skarn zone, suggesting that the mechanism of ore deposition was controlled to some degree, by oxidation and reduction reactions within the silicate assemblages (Einaudi, 1981). Other causes of deposition include falling temperature and the neutralization of the ore fluid at the marble contact. Scheelite is the only major ore mineral that commonly forms during the early prograde stage. The deposition of this mineral is controlled by the activity of calcium in the fluids.

2.0.3 MINERAL EQUILIBRIA AND SKARN FACIES

Isotopic and fluid inclusion data (Taylor and O'Neil, 1977) indicate that skarn fluids are water-rich, H_2O-CO_2 mixtures, in which X_{CO_2} is often less than 0.1 during contact metamorphism and metasomatism. Comparisons of mineral equilibria on T- fO_2 and T- X_{CO_2} diagrams with actual skarn assemblages suggest that during the early skarn stage fO_2 and X_{CO_2} are not buffered by local mineral equilibria (Burt, 1971), which would otherwise

produce invariant assemblages. The buffering capacity of early mineral assemblages is overcome by fluids in which fO_2 and XCO_2 are controlled by the oxidation state of the intrusive, or the rock through which they have travelled. During retrograde alteration of the skarn, fO_2 and XCO_2 may be locally controlled by the breakdown of earlier skarn silicates.

The externally controlled variables, T , P , XCO_2 , fO_2 and sometimes fS_2 , define the skarn 'facies' during the prograde stages. Several types of phase diagrams are commonly used to represent phase equilibria in skarns, including T - fO_2 , T - XCO_2 and fO_2 - fCO_2 . Many skarn reactions are not isochemical and cannot be represented on these diagrams; however, they may be used to define the stability limits of the skarn assemblages. Reactions in the system $Ca-Al-Si-C-O-H$, involving such common skarn minerals as grossular, anorthite, zoisite, wollastonite and prehnite, can be used to place limits on temperature and fluid composition (XCO_2). This system is applied to assemblages in the MARN deposit in Chapter 5.

There is a tendency for many authors to simplify skarn assemblages to the end member $Ca-Fe-Si-C-O$ and $Ca-Mg-Si-C-O$ systems, corresponding to iron-rich calcic skarns and magnesian skarns respectively. Most skarn silicates are not end member compositions, and the effect of progressive solid solution must be considered. Decreasing the activity of hedenbergite in the pyroxene effectively increases the stability of pyroxene-bearing assemblages. This is demonstrated in $\log fO_2$ - $\log fCO_2$ diagrams for the MARN skarn assemblages in chapter 5.

The concept of skarn 'facies' is well illustrated by the tungsten deposits of Japan (Burt, 1972; Shimazaki, 1980; Sato, 1980). Molybdenum-bearing scheelite (10-20 mole% Mo) is associated with andradite, zoisite and magnetite in a similar manner to the oxidized tungsten skarns of California (Kerrick, 1977). Low-molybdenum scheelite occurs in pyrrhotite-rich deposits, associated with silicates low in ferric iron, such as hedenbergite. All these types are in regions of ilmenite-bearing granitoids, which are believed to represent reduced magmas. In contrast, the 'oxidized', molybdenoscheelite-bearing skarns are associated with magnetite granitoids. The correlation between mineral assemblages in skarns, and the apparent oxidizing conditions of the intrusive confirm that oxygen fugacity is largely externally controlled during the prograde

skarn formation.

2.0.4 GOLD-BEARING SKARNS

Gold is a frequent, minor constituent of skarns, often being produced as a byproduct of copper or lead-zinc smelting. Copper skarns are often enriched in both gold and silver, in contrast to the consistently low values from many tungsten skarns. Although skarns containing gold are not uncommon, few are discussed in detail in the literature.

Gold may be present in auriferous sulphides, as the native metal, as tellurides, or more rarely as electrum. Other elements that are often enriched with gold are Fe, S, Cu, Ag, Zn, Pb, Mo, As, Bi and Te (Boyle, 1979). In the Nickel Plate and French mines of the Henley district, British Columbia, the principle gold-bearing phases are auriferous arsenopyrite and native gold. Other minerals in the ore association include chalcopyrite, pyrrhotite, covellite, molybdenite, safflorite, native bismuth, hedleyite (Bi_4Te_6) and joseite ($\text{Bi}_{1-x}\text{Te}_{1-x}\text{S}$). These two mines grade approximately 13.7ppm Au and 1.2ppm Ag. Auriferous chalcopyrite associated with cobalt-bearing pyrite and arsenopyrite are characteristic of many calcic iron skarns (Meinert, 1984).

In Japan, there is a clear correlation between the Au/Cu ratio of skarn deposits and the type of associated intrusive (Shimazaki, 1980). Considerable amounts of gold have been produced as a byproduct of copper production from skarns related to magnetite-bearing intrusives. Those associated with ilmenite granitoids show significantly lower total gold values, and lower Au/Cu ratios. This relationship suggests that more oxidizing fluids, such as those emanating from magnetite-bearing intrusion, are more favourable for the transport of gold than reduced conditions associated with ilmenite granitoids. An oxidized skarn environment might also trigger deposition of gold from a reduced fluid. In conclusion, it appears that gold is more abundant in skarns containing oxidized mineral assemblages such as magnetite and andradite, and is rare or absent in the reduced tungsten skarns of Japan, and those of the Yukon (Dick and Hodgson, 1982).

Table 2.1

Characteristics of the major skarn types.

	CALCIC FE SKARNS	MAGNESIAN FE SKARNS
Tectonic environment and igneous association.	Diorite-gabbro in island-arc volcano-sedimentary sequences.	Cordilleran granodiorite to quartz monzonites.
Average grade and tonnage.	5-200 MT, 40% Fe	5-100 MT, 40% Fe
Metal association.	Fe (Cu, Co, Au, Ni, Zn, Ag, Mo)	Fe, Cu, Zn
Mineralogy: Prograde	Grandite, salite epidote, magnetite actinolite, chlorite ilvaite, quartz calcite	Forsterite, diopside Calcite, spinel, magnetite humite phlogopite serpentine
Retrograde	magnetite, chalcocopyrite cobaltite pyrrhotite	magnetite, pyrite pyrrhotite, chalcocopyrite sphalerite
Ore		

Table 2.1 cont.

Tectonic environment and igneous association.	CU SKARNS	W SKARNS
	Calcalik granodiorite to quartz-monzonite of continental margin orogenic belts. Mineralized porphyritic stocks in subvolcanic environments or deeper level and barren stocks.	Continental margin, syn- to late orogenic quartz diorite to monzonite.
Average grade and tonnage.	a. porphyritic stocks: 50-600 MT, 1% Cu b. barren stocks: 1-50 MT	0.1-2 MT, 0.7wt% WO ₃
Metal association.	Cu, Mo, (W, Zn)	W, Mo, Cu, (Zn, Bi)
Mineralogy: Prograde	Andradite, garnet salitic pyroxene wollastonite	a. 'Oxidized': andradite, diopside zoisite, wollastonite b. 'Reduced': hedenbergite, grossular, wollastonite
Retrograde	Actinolite, chlorite	hornblende, biotite, plagioclase, epidote
Ore	chalcocopyrite, bornite, pyrite, hematite, magnetite	scheelite, molybdenite, chalcocopyrite, pyrrhotite, pyrite

Table 2.1 cont.

	MO SKARNS	SN SKARNS
Tectonic environment and igneous association.	Late orogenic, continental margin, quartz monzonite to granite	Late to post orogenic granites
Average grade and tonnage.	0.1-2.0 MT, 0.15% MoS ₂	0.1-3.0 MT, 0.15% Sn
Metal association	Mo, W, (Cu, Bi, Zn, W, Pb, Sn, U)	Sn, Fe, (Be, W, Mo)
Mineralogy: Prograde	Hedenbergitic pyroxene grandite, wollastonite quartz	a. Magnesian skarn: Spinel, fassaite forsterite, phlogopite, humite, magnetite b. Calcic skarn: malayite, grandite idocrase, datolite
Retrograde	Hornblende, actinolite, epidote fluorite, chlorite	fluorite, cassiterite, micas chlorite
Ore	Molybdenite, scheelite, bismuthinite, pyrite, chalcocopyrite	cassiterite, arsenopyrite, stannite, pyrrhotite, sphalerite

Table 2.1 cont.

PB-ZN SKARNS

Continental margin, syn- to late orogenic
granodiorites, granites or diorite-syenite.
Skarns are typically distal to the intrusive.

0.2-3.0 MT, 9%Zn, 6% Pb, 5oz/t Ag

Zn, Pb, Ag, (Cu, W)

Mn-pyroxene, bustamite, andradite,
wollastonite

Mn-ilvaite, chlorite, epidote, Mn-actinolite

Sphalerite, galena, chalcopyrite,
arsenopyrite

Tectonic environment and igneous
association.

Average grade and tonnage.

Metal association

Mineralogy:
Prograde

Retrograde

Ore

3. THE GEOLOGY OF THE MARN CLAIMS

3.1 INTRODUCTION

The MARN claims cover part of the northwest contact of the Mount Brenner Stock with three sedimentary units: the Devono-Mississippian Formation (DMSc), the Permian Tahkandit Limestone, and a formation of Jurassic age. Two mineralized skarn bodies on the northern and southern margins of a sill-like extension of the Mount Brenner Stock have been the focus of a three year drilling program by Noranda Exploration Ltd. The northern skarn, in the Mini-Grid area (Fig. 3.1), has been delineated entirely by drilling while the southern skarn is well exposed in Mineral Gully, but is poorly delineated beneath the sill. Excellent exposure of the sedimentary units occur 3km south of the sill, and allow the study of the three formations beyond the thermal aureole of the Mount Brenner Stock. In the following discussion, this area is referred to as the Southern Claims. The three sedimentary units are described briefly below.

3.1.1 THE DEVONO-MISSISSIPPIAN FORMATION (DMSc)

This formation has been mapped as the Road River Formation (Tempelman-Kluit, 1969). On the MARN claims, the units below the Tahkandit limestone are more clastic than typical Road River Formation and have been tentatively assigned to a younger Devono-Mississippian Formation (Biczok, 1981). There is no local name for this unit, although it may be equivalent to the Canol or Imperial Formations (Biczok, 1981).

The rusty weathering DMSc includes argillaceous quartzites, shales and conglomerates. A unit of breccias within the metamorphic aureole north of Fireweed Creek contains fine and medium-grained volcanic and intrusive fragments. A sequence of cherts and black shales beneath the limestone on the Southern Claims may be part of the Road River Formation. As a result of metamorphism, no chert is present the northern region of the claims, where the DMSc consists of quartz-rich graphitic, biotite and cordierite hornfels.

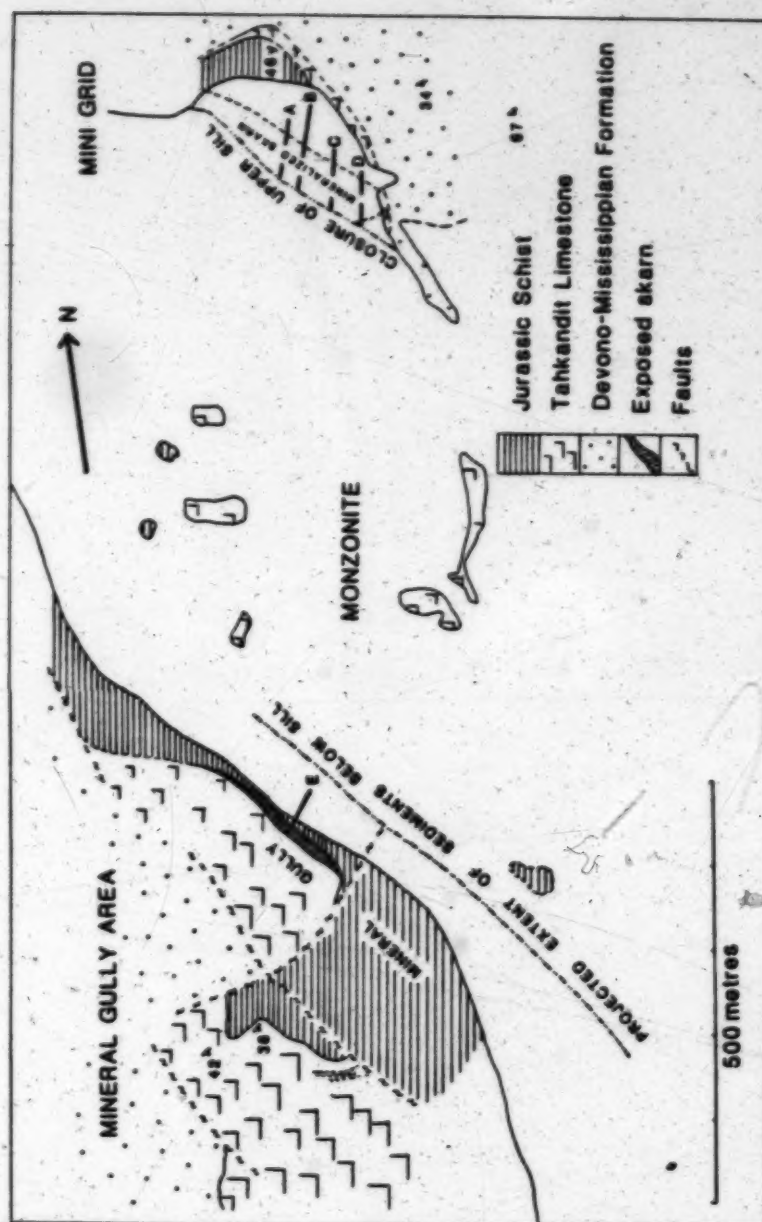


Figure 3.1. The geology of Mineral Gully and Mini-Grid areas.

3.1.2 TAHKANDIT LIMESTONE

This Permian age unit is the major host of skarn mineralization. It reaches a maximum thickness of 25 to 30 metres on the Southern Claims, thinning out to 10 metres in the Mini-Grid area. The Tahkandit Limestone has been correlated with a Permian sequence of conglomerates and limestones in East Central Alaska that reach 180 metres in thickness (Tempelman-Kluit, 1970). In the Tombstone area, the maximum thickness is 35 metres. Three divisions have been recognised: an upper massive limestone unit up to 17 metres thick, containing minor chert lenses; a middle limestone with 7 metres of interbedded black chert; and a lower limestone containing detrital chert beds and lenses. The entire sequence is fossiliferous. Dolomites represent less than 5% of the carbonates.

On the Southern Claims, the lowest unit is a nodular cherty limestone with minor, chert pebble lenses. The middle unit contains numerous, discontinuous chert pebble horizons. A banded, cherty limestone, similar to middle unit, outcrops in Mineral Gully, where metamorphic recrystallization has obscured many of the primary textures. The highest limestone unit on the Southern Claims is a massive, coarse-grained limestone. A chert pebble conglomerate is present near the upper contact with the Jurassic Schist.

Recrystallization and skarnification of the limestone in Mini Grid and Mineral Gully, make a comparison between these areas and the limestone of the Southern Claims difficult. However, a 4 metre-thick, basal pebble conglomerate similar to those seen on the Southern Claims, is recognisable in DDH-27 and in the outcrop above Mini-Grid. Textures in unaltered marble from the trenches on the Mini-Grid suggest that chert nodules were present in the limestone here also.

3.1.3 JURASSIC SCHIST

In the Tombstone area, no formation name is given to the Jurassic rocks, which have been separated into two units. Tempelman-Kluit (1970) considered these two units to be a single, structurally repeated formation. The lower of the two horizons may be traced into the Keno Hill and Galena Hill area, where it has been given the local name, 'Lower Schist'. In order to distinguish the Jurassic-age rocks on the MARN claims from the Devonian-Mississippian Formation, the younger unit will be informally referred to as the Jurassic Schist in this report. This unit is made of up to 500 metres of black slates,

feldspathic greywackes, argillites and siliceous phyllites. On the MARN claims, the unit is represented by rusty weathering, fine-grained, impure and sometimes graphitic quartzites. In general these rocks are less graphitic than the Devono-Mississippian Formation. A thin, polymict conglomerate was intersected in several drill holes at the base of the Jurassic Schist.

3.1.4 INTRUSIVES

The Mount Brenner Stock is a differentiated and zoned monzonitic intrusion. Lambert (1966) described a concentric sequence of zones in the intrusion, representing increasing differentiation inwards. The zoning from an outer augite-biotite monzonite, to hornblende monzonite and finally to quartz monzonites, represents a trend from quartz-undersaturated to quartz-oversaturated compositions.

The MARN claims include a sill-like body which extends northwestwards from the main stock. The dominant rock-type both of the sill and the margin of the stock in this area is augite-biotite monzonite. Multiple phases of injection are seen in the main stock, where small finer-grained or leucocratic dykes cut the medium-grained monzonite. Dioritic material intersected in some drill holes makes up only a small portion of the intrusive.

Xenoliths of all three sedimentary formations are abundant, particularly in the central region of the sill (PLATE 1a). A large, slightly skarnified limestone body within the sill appears to be almost continuous with the limestone of Mini-Grid where it is visible in the rugged cliffs that form the outcrop of the main sill.

Biczok (1981) describes two thicker 'ribs' of intrusion along the northern and southern margins of the sill. Between these, the sill appears to thin, corresponding to the region of the greatest density of xenoliths. Numerous minor monzonitic to dioritic sills were encountered during drilling on the Mini-Grid, all of which are texturally and compositionally similar to the main sill. On the southern margin of the sill there is a greater variety of intrusive rocks.

1. MONZONITES: Medium-grained, augite-biotite monzonites make up most of the sill that separates the two skarn bodies. Quartz is not abundant, forming less than 5% of the rock. Salitic augite (Fig. 3.2) and biotite are the most abundant mafic minerals, typically accounting for 45% of the rock. Occasionally, pyroxene may form as much as 70% of the

PLATE 1

**PLATE 1a. View of the monzonite sill looking northwest from the main Mount
Brenner Stock.**

**PLATE 1b. View of the Mineral Gully area looking towards the north. The two
important normal faults are shown.**



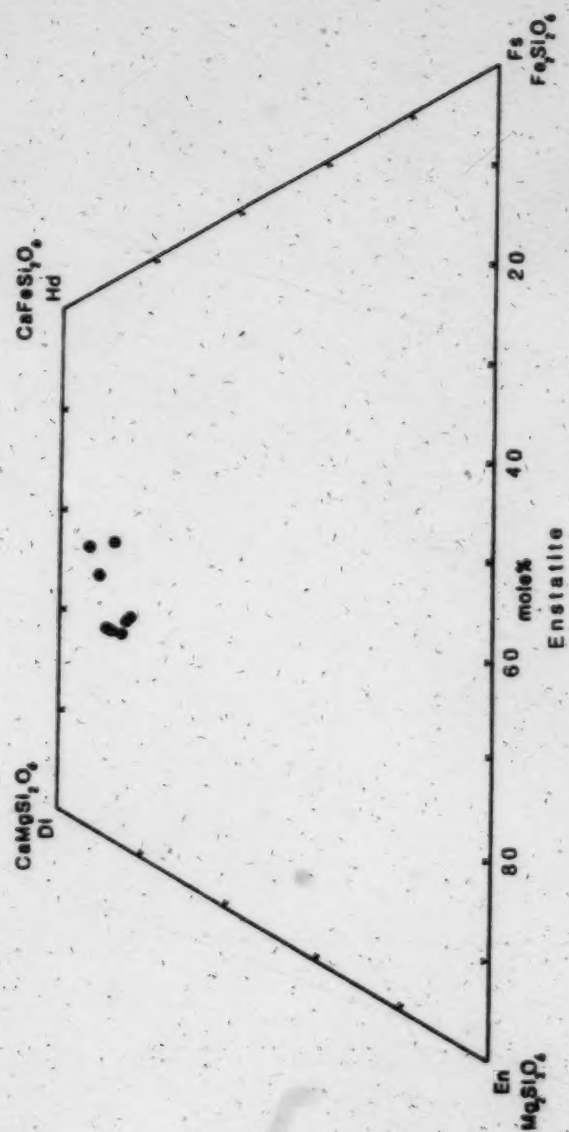


Figure 3.2. Compositions of augites from the monzonite sill.

monzonite. Locally, monzonite grades into more porphyritic dioritic material in which 90% of the feldspars may be plagioclase. Green amphibole is usually present as a minor alteration along the fractures and grain boundaries of pyroxenes. Occasionally hornblende is a major phase.

In the typical pyroxene-biotite monzonite, plagioclase and alkali-feldspar are present in approximately equal amounts. Large orthoclase grains typically enclose smaller, subhedral andesine (Ab_{50}) laths. Orthoclase is commonly perthitic and occasionally forms a myrmekitic intergrowth with plagioclase. Biotite occurs as small grains included within the cores of the pyroxenes and as larger independent flakes. The igneous biotites are considerably richer in titanium than their metamorphic counterparts (Appendix 1, B13).

Ilmenite, magnetite and titaniferous magnetite have been observed. Grains of unexsolved titaniferous magnetite occur in the same sample as magnetite with exsolved ilmenite. Ilmenite is the most common, primary, igneous opaque phase and is often altered to sphene. Pyrite, pyrrhotite and chalcOPYrite are abundant in the monzonites adjacent to the skarns, but these minerals show replacement and veining textures and are probably related to the skarn events.

Molybdenum occurs in the margin of the main intrusive body where it forms veins with amphibole, feldspars and quartz. These veins may be related to the skarn-forming events, representing a form of endoskarn within the intrusive. A thorium-uranium silicate was observed in monzonite during a qualitative run on the microprobe.

The textures of two pyroxene-hornblende diorite dykes near Mineral Gully show a replacement relationship between the two major mafic minerals. Zoned hornblende, plagioclase and pyroxene phenocrysts are up to 0.2 cm long. The matrix is composed of fine-grained plagioclase, anhedral amphibole and sphene. Relict pyroxene is present in many of the larger hornblende phenocrysts, while other pyroxene grains show only minor replacement.

2. QUARTZ-SCAPOLITE DYKES: Very close to the two diorite dykes mentioned above are a number of small, cross-cutting leucocratic dykes. Their mineralogy is variable, containing up to 40% quartz and equal amounts of plagioclase and K-feldspar. Clinopyroxene is the only mafic mineral present, typically forming less than 10% of the rock. Patchy development of coarse, radiating scapolite associated with calcite may make

up 60% or more of these dykes. A 1 cm wide, light-green pyroxene skarn is developed in the wollastonite marble adjacent to these felsic dykes. This bears no relationship to bedding-controlled, hedenbergitic skarn which is present in the same outcrop. These dykes post-date the main skarn-forming event.

3. SYENITE SILL: A major fine-grained, slightly porphyritic syenite sill outcrops in Mineral Gully, and was intersected in DDH-15. This 3 metre thick sill is only present on the north side of Mineral Gully where it runs subparallel to bedding for about 200 metres. It post-dates the main skarn and cross cuts the monzonite sill above Mineral Gully.

The ground mass of the syenite, consists of very fine-grained K-feldspar. The phenocrysts are plagioclase, K-feldspar and brown hornblende. Near the margin of the sill, quartz and calcite almost completely replace the phenocrysts. Actinolite is extensively developed in the adjacent skarn; however, xenoliths of pyroxene skarn in the margins of the sill indicate that it post-dates the formation of the skarn.

3.1.5 STRUCTURE

The Tahkandit Limestone dips uniformly eastwards at 10 to 20 degrees over most of the area covered by the MARN claims. Adjacent to the sill margins, the bedding dips in towards the intrusive contact, defining a synclinal structure. A series of normal faults along Fireweed Creek have downfaulted the limestone towards the stock.

The contacts of the Tahkandit Limestone with both the Devono-Mississippian Formation and the Jurassic Schist are unconformable. Very tight isoclinal folding observed in the Jurassic Schist in Fireweed Creek, suggests that a thrust fault may follow the lithological boundary. Biczok (1980) describes similar folding across the Southern Claims, and into the Mount Brenner Valley. Early Cretaceous thrust faulting is a feature of the Tombstone area, although it has not been recognised in the area of the MARN claims.

3.2 THE GEOLOGY OF THE MINI-GRID AREA

Between 1980 and 1983, twenty-three diamond-drill holes were sited on the northern edge of the large monzonite sill, in the area known as Mini-Grid (Fig.3.3). Skarn development and mineralization occur entirely beneath an upper sill, while many of the drill-holes were terminated in a lower monzonite body. Unmineralized and unskarnified

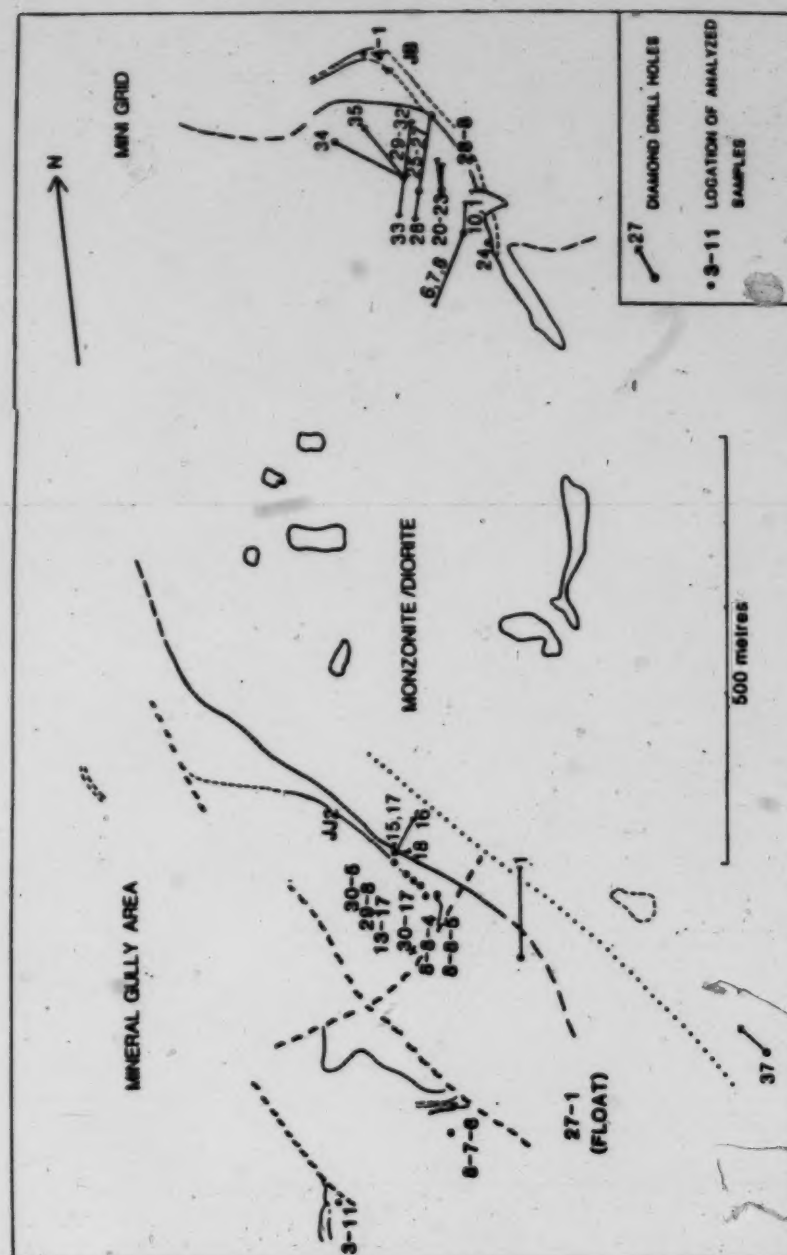


Figure 3.3. The location of sampled drill holes and exposures.

marble outcrops on the ridge crest, 50 metres from the igneous contact. Numerous small sills, which are intersected in the drill-holes, rarely continue to the surface.

The skarn horizon is not continuously mineralized, neither does it follow a regular or consistent pattern. Sections through the margin of the sill are shown in Figures 3.4-3.7. The interpolation of the skarn and the mineralization between drill-holes is speculative. The location of the skarn horizon appears to bear some relationship to lithological boundaries. Mineralized skarn developed in the Tahkandit Limestone immediately below the Jurassic Schist is illustrated in Figure 3.4; however, this same horizon is barren in Figures 3.5 and 3.7. In Figure 3.7, high-grade mineralization occurs within the quartz-rich, DMSc Formation below a middle monzonite sill, while the lower contact of the limestone hosts a more weakly developed skarn horizon. No replacement of the Jurassic Schist by skarn is seen.

The convergence of the upper and lower sills, illustrated in Figures 3.4-3.7, defines the southern limit of mineralization. Erosion truncated high-grade mineralization that is exposed in two trenches on the eastern side of the deposit (Fig. 3.8). The extent of skarn westwards is unknown, although none has been found on the western side of the ridge. The limit of mineralization northwards is not well constrained; however, Barren and unmineralized, wollastonite-bearing skarn was intersected in DDH-27 (Fig. 3.6). This intersection is approximately 60 metres from the projected truncation of the limestone by the lower sill and represents a maximum extent of mineralization.

Figures 3.4, 3.5 and 3.6 illustrate the extent of intense, late alteration of the Tahkandit Limestone. The altered marble is characteristically composed of friable quartz and calcareous debris. Locally, both the marble and monzonite are affected by hematitic, limonitic and argillic alteration. Generally, alteration is more strongly developed below the skarn horizon. In section 3.5, the mineralized skarn is located in the lower portion of the Tahkandit Limestone, beneath unaltered wollastonite marbles. Alteration shown in this section may be attributed to the effects of a normal fault which is inferred from the presence of sheared debris in two drill-holes. A similar structure may account for the greatly increased thickness of Tahkandit Limestone seen in Figure 3.4. Chalcocite, cuprite, malachite and chrysocolla occur sporadically in veins within the altered limestone and monzonite. Similarly, coarse calcite veins occur both in the altered marbles and in the

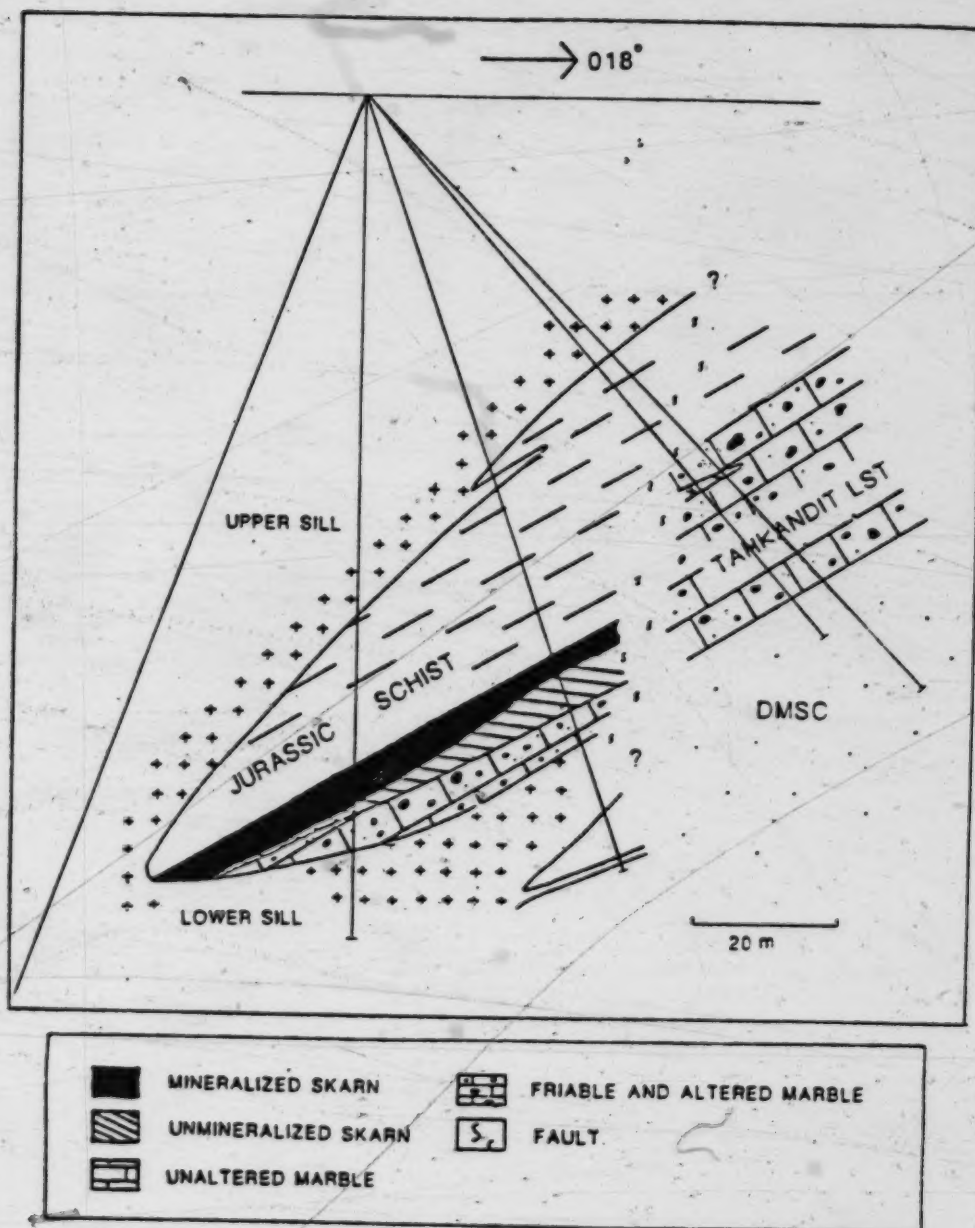


Figure 3.4. Section A through the Mini-Grid skarn.

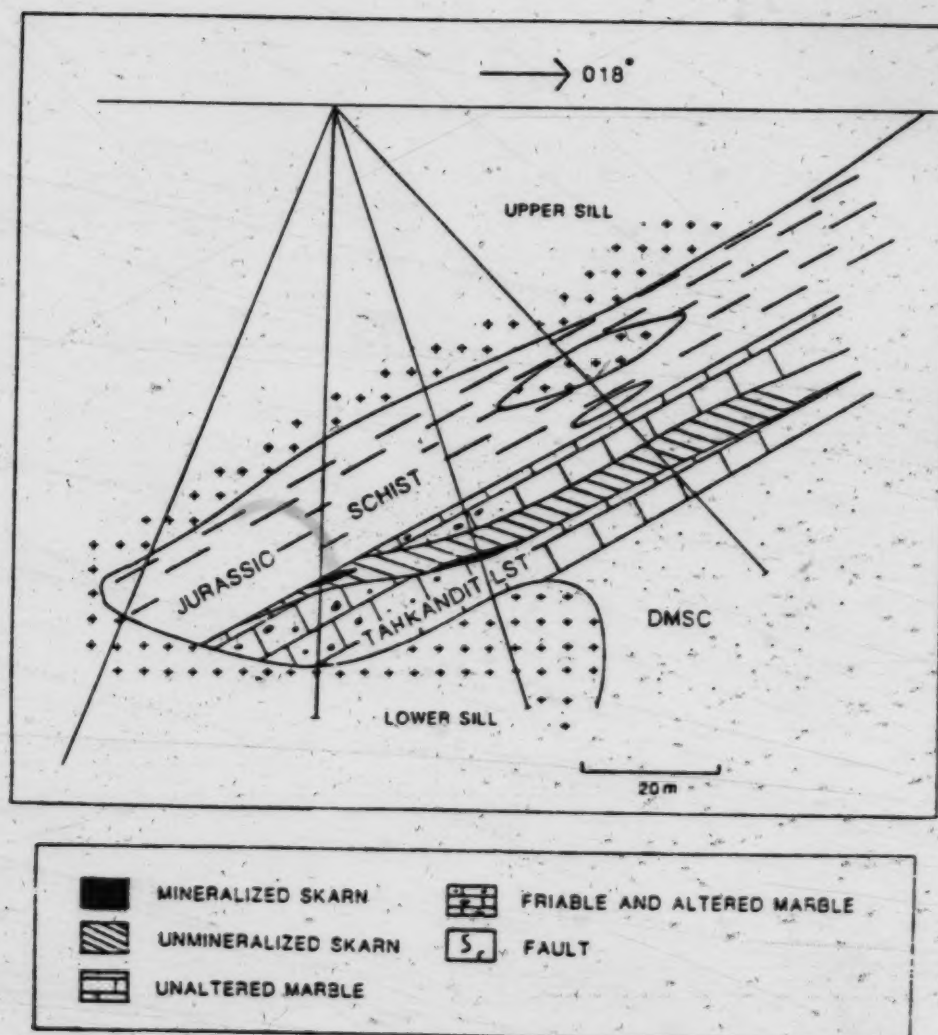


Figure 3.5. Section B through the Mini-Grid skarn.

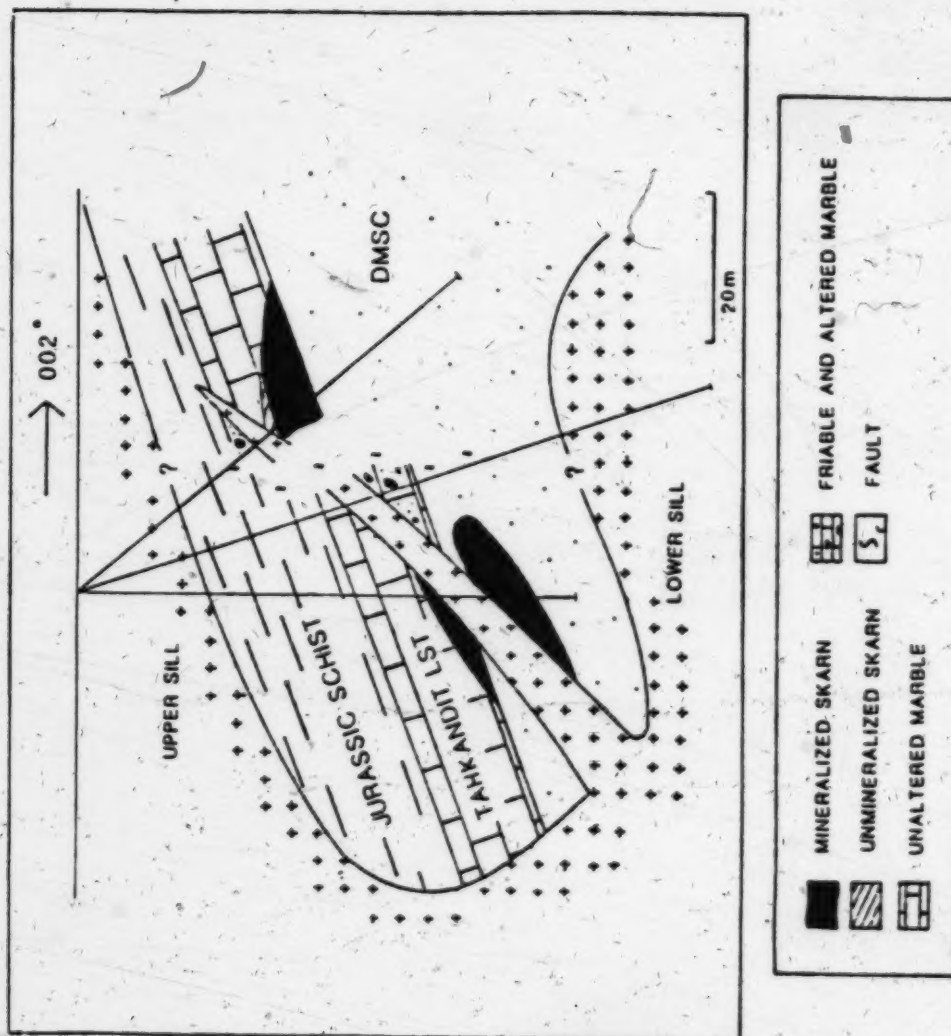


Figure 3.6. Section C through the Mini-Grid skarn.

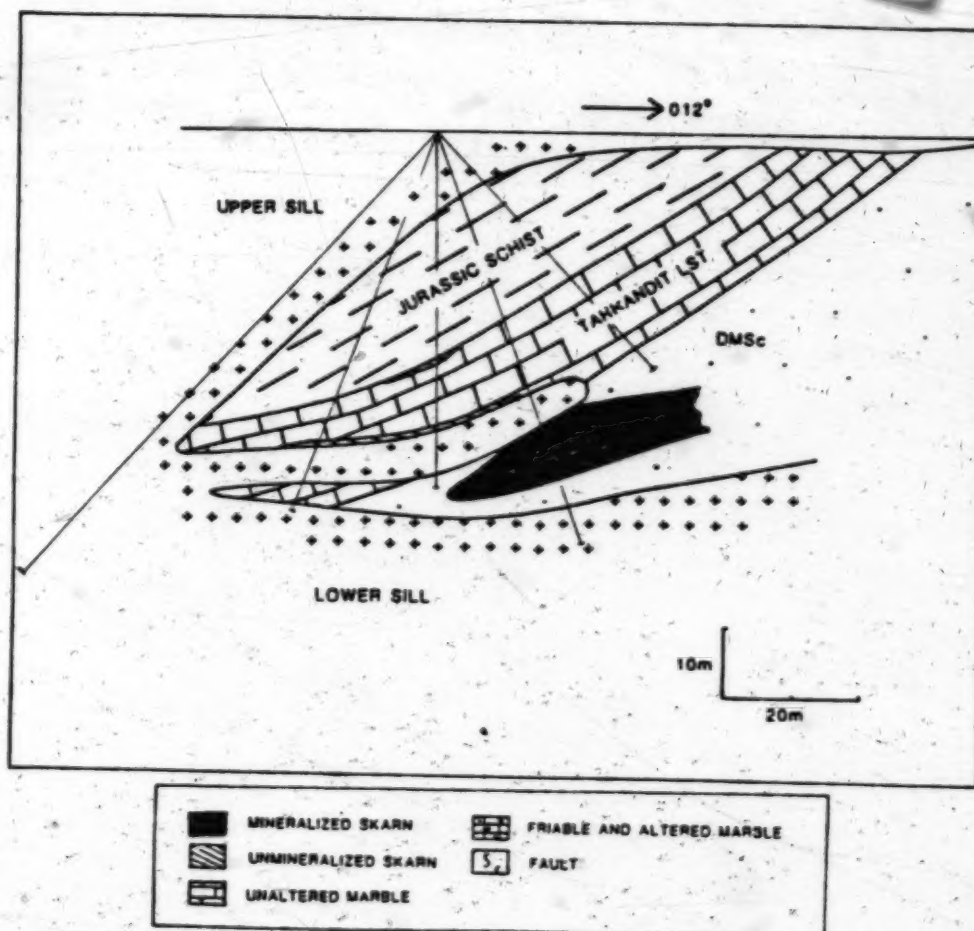


Figure 3.7. Section D through the Mini-Grid skarn.

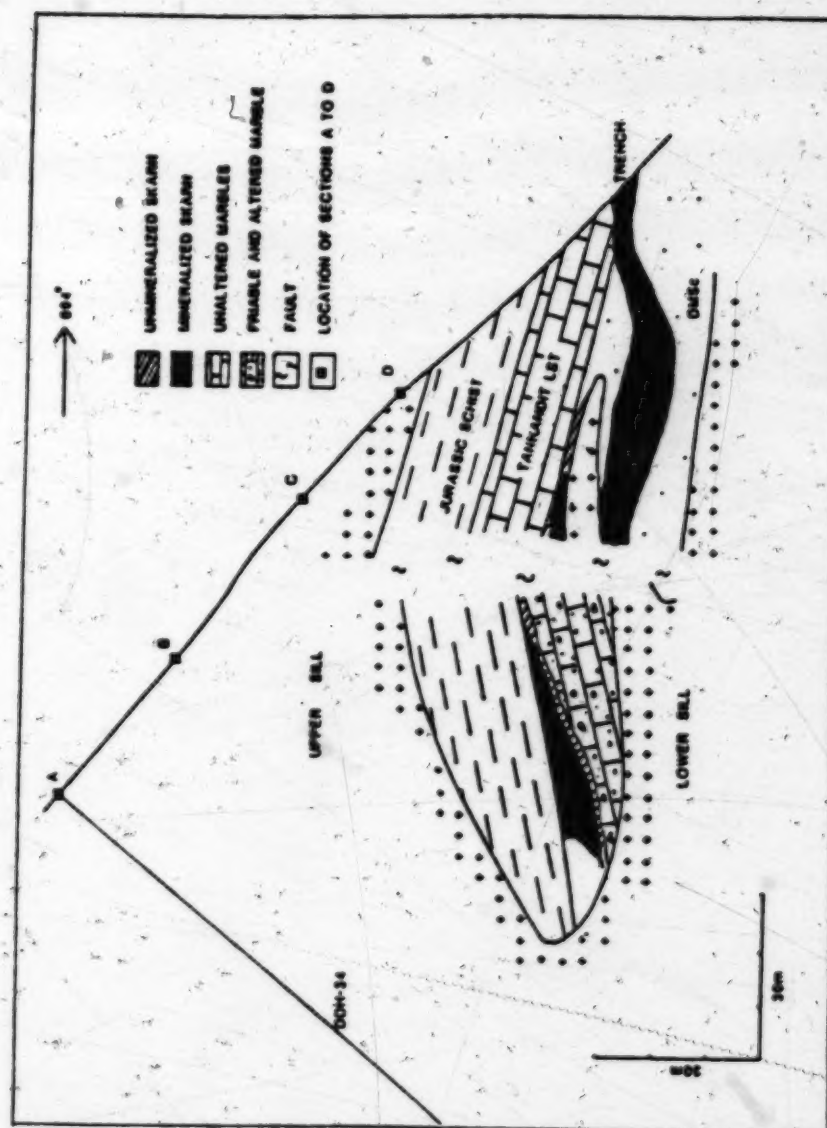


Figure 3.8. East-West section through the Mini-Grid skarn approximately parallel to the closure of the Upper Sill.

intrusive in contact with the Tahkandit Limestone.

In summary, the main mineralized skarn horizon defines a region that lies subparallel to the intrusive contact. Barren, wollastonite-bearing skarn forms an outer zone around the dark-green, and sometimes mineralized inner zone. The skarn is constrained between an upper and a lower monzonite sill, while smaller, intermediate sills also appear to have had some control on skarn formation. Both the skarn itself, and the mineralization, are discontinuously developed, and somewhat unpredictable. Although most of the skarn is hosted by the Tahkandit Limestone, some of the highest-grade mineralization occurs in identical skarn in the DMSc Formation.

3.3 THE GEOLOGY OF MINERAL GULLY

Dark-green skarn is exposed over a distance of nearly 200 metres in the upper part of Mineral Gully. Unfortunately drilling in this area was very limited, and little is known of the extent of skarn development beneath the sill.

Two major, normal faults cut the hillside north of Lake Scolville into four sections (Fig. 3.1)(Plate 1b). The NE-SW trending fault is exposed in Mineral Gully where it marks the extent of the skarn outcrop. Jurassic Schist has been downthrown on the southeast side, bringing it into contact with the limestone. DDH-1 intersected slightly skarnified and mineralized limestone beneath 110 metres of Jurassic Schist on the downthrown side of this fault. A reconstruction from DDH-17 and DDH-1 indicates a displacement of about 100 metres. The limestone is dragged down along the fault; however, there is no evidence that the fault acted as a conduit for skarn fluids, and it probably postdates the skarn formation. The NW-SE trending fault that passes between Mineral Gully and a second valley 250 metres to the west, displaced the sediments downwards on the southwest side, towards the intrusive.

In the northeast and southwest quadrants defined by these two faults, marble is well exposed, dipping almost parallel to the hillside at 40 degrees and slightly in towards the sill contact. Evidence of primary chert banding is very clear in the wollastonite and wollastonite-diopside marbles, where quartzite horizons give it a strongly bedded appearance.

The Jurassic Schist and Devono-Mississippian Formation are very similar in appearance, forming biotite-porphyroblastic quartzites and cordierite hornfels. Strong planar fabric is often defined by biotite orientation. No sedimentary structures are seen in either of these formations in the Mineral Gully area.

Numerous sills and dykes in this area were described earlier. Pale-green diopsidic contact skarns are often developed at the margins of small monzonite sills. Characteristically these sills are subparallel to lithological boundaries.

Mineral Gully deeply dissects the hillside close to the edge of the large monzonite sill. The creek bed in the upper half of the gully marks the edge of the massive, pyroxene skarn outcrop. DDH-15, 16 and 17 intersected skarn identical to that in outcrop (Fig. 3.9). None of these drill holes intersected the DMSc Formation.

The skarn is developed in the upper part of the limestone horizon directly below the Jurassic Schist (Plate 2a). In outcrop the contact is not clear cut, suggesting some degree of skarn development in the quartz-rich unit. Figure 3.10 illustrates the strong control that bedding had on skarn formation.

At its greatest thickness, the skarn forms an upper horizon which is cut by the syenite dyke previously described. The lower part of this horizon converges with a second, smaller lens downstream. Continuous, low-grade pyrrhotite and chalcopyrite mineralization is present below the syenite sill and in patches above. The smaller, lower lens is barren.

In the creek bed, pods and lenses of barren skarn show sharp contacts with the adjacent wollastonite marble. These are commonly confined to the marble horizons between quartz-rich beds. The shape of these lenses suggests that movement of the skarn-forming fluids was parallel to the present creek bed (Plate 2b).

Dark-green skarn occurs up to 150 metres beyond Mineral Gully. Numerous veinlets of similar skarn material occur throughout the marbles up to 250 metres from the Mineral Gully outcrops. These small cross-cutting features probably follow healed fractures.

Up slope from the main outcrops, the skarn pinches out (Fig. 3.10). The appearance of the skarn changes from massive and dark-green rocks to layered wollastonite and pyroxene skarn. This banding is reminiscent of the siliceous and

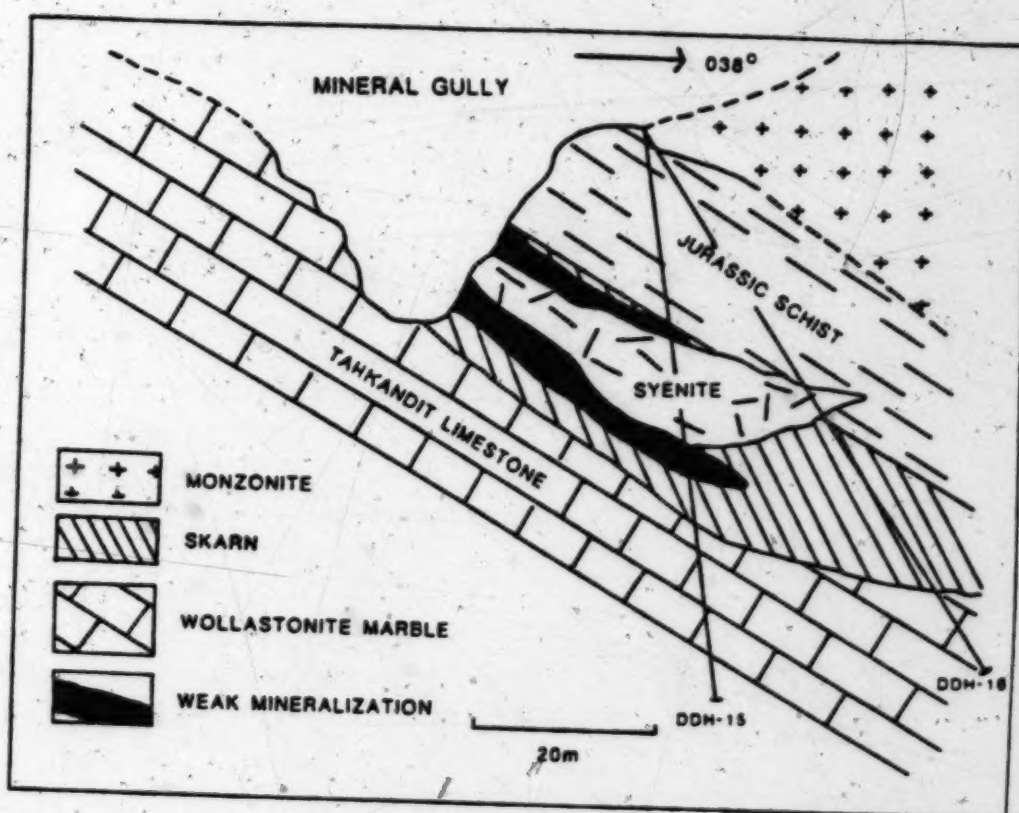


Figure 3.9. Section through the massive skarn horizon in Mineral Gully.

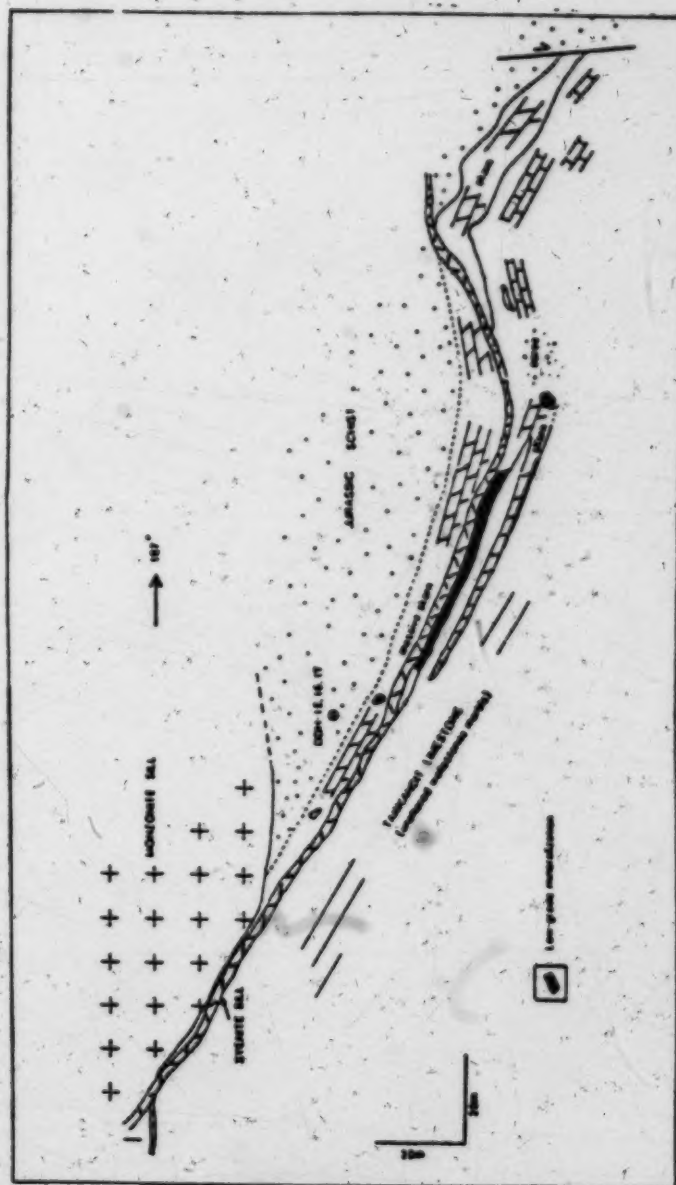


Figure 3.10. Longitudinal section of the northern side of Mineral Gully, showing the location of the skarn lenses and the very-low-grade mineralization.

PLATE 2

PLATE 2a. Massive pyroxene skarn below the Jurassic Schist (JS) in Mineral Gully, showing remnants of the wollastonite marbles.

PLATE 2b. Hedenbergitic skarn lens in the creek bed in Mineral Gully. Thin, grey quartzite horizons (Q) are visible in the marbles. The fine-grained syenite sill is in the lower right of the picture.



COLOURED PICTURES
Images en couleur

calcareous layering of the unaltered limestone.

DDH-37 (Fig. 3.3) was drilled in the hope of intersecting further mineralized skarn down-dip and at a deeper level beneath the sill. This hole intersected 5.6 metres of unmineralized garnet-wollastonite-pyroxene skarn beneath 215 metres of intrusives. No other sedimentary rocks were found. The intrusives were mainly medium-grained augite monzonites, but also contained finer-grained and more leucocratic sills.

In contrast with the Mini-Grid drill core, the skarn on the southern margin of the monzonite sill, shows little, if any, limonitic alteration or secondary copper mineralization.

3.4 CONDITIONS OF CONTACT METAMORPHISM

Tempelman-Kluit (1970) proposed that the erosion level of the Mount Brenner and Tombstone Stocks seen today is close to the roof of the original intrusion. Assuming that a single stratigraphic succession was present, the thickness of the sediments at the time of intrusion in the early Late Cretaceous would have been 1000 metres, corresponding to a pressure of 0.35 KBars. However, if the overthrusting that is present in the region to the south, continued into this area, the depth of emplacement might have been considerably greater. Tempelman-Kluit (1970) suggested that thrusting might have increased the thickness of the sediments to 3300 metres (<1 Kbar). Clearly the pressure attained during contact metamorphism cannot be estimated by this method.

Temperature and pressure conditions during the emplacement of the Mount Brenner Stock, are reflected in the mineral assemblages of the Jurassic Schist and DMSc adjacent to the intrusive. Both these units are dominated by biotite-rich quartzites and biotite-quartz schists. The assemblages include the following:

- Q-bt-gra-crd-plag
- Q-gra-sill-bt-andalusite-musc
- Q-gra-crd-bt-musc-plag
- Q-crd-bt-gra-rutile-po
- Q-bt-sill-crd-gra-K feld-rutile
- Q-bt-sill-tourm-crd-musc-plag-py-gra-rutile
- Q-bt-alm-plag-po-gra-rutile

Q-bt-alm-ilrn-rutile-sphene

Graphite and fibrolitic sillimanite are almost ubiquitous in rocks close to the intrusion. Andalusite occurs only in one sample, forming an intergrowth with prismatic sillimanite. Andalusite-bearing rocks probably formed at a lower temperature than those with sillimanite as the only aluminium-silicate. The triple point of the aluminium-silicate polymorphs of Holdaway (1971), gives a maximum pressure of 3.8 Kbars for the thermal aureole of the Mount Brenner Stock in the MARN area.

In the Tahkandit Limestone, the skarn assemblage, wollastonite-anorthite (An_{100}) is stable between 600°C and 800°C (Gordon and Greenwood, 1971). 600°C is used tentatively as a lower temperature limit of early metamorphism, although fluid circulation during skarn development tends to smooth out the thermal gradient close to the intrusive.

There is no evidence that melting occurred in the sedimentary units, although migmatitic textures are seen in some deeper holes near Lake Scolville. Therefore, the maximum temperature reached during metamorphism in the vicinity of the skarns was probably below the granite solidus (Fig. 3.11).

Temperatures and pressures may be further constrained by mineral equilibria (Fig. 3.11). In graphite-bearing systems, the mole fraction of water (X_{H_2O}) in the metamorphic fluids is approximately 75% of the total pressure between 600° and 700°C (Ohmoto and Kerrick, 1977) assuming that fluid pressure is equivalent to total pressure. The effect of decreasing X_{H_2O} from 1.0 is to bring some of the equilibria in Figure 3.11 to lower temperatures and pressures. The assemblages biotite-sillimanite-quartz and K feldspar-sillimanite restrict the P-T range to the shaded area in Figure 3.11.

In conclusion, the early contact metamorphic event reached peak temperatures of 600°C to 700°C in the inner thermal aureole. The pressure, though not well constrained by mineral assemblages, is in the range of 2.0 to 3.8 Kbars. 2 kbars is typical of many deeper-level skarn environments, and will be used in further discussions.

4. PETROLOGY AND PARAGENESIS OF THE SKARNS

4.1 INTRODUCTION

The contact metamorphic event associated with the emplacement of the monzonite sill was followed by a series of stages of skarn formation in the Tahkandit Limestone. Barren, wollastonite and a grossular-bearing skarn contrasts with mineralized iron-rich pyroxene skarn. Both of these types of skarn occur on the north and south sides of the sill; however, their distribution is insufficiently known to allow the identification of a clear zonal pattern. The barren skarn located in DDH-27, and the mineralized pyroxene skarn of Mini-Grid may represent outer and inner zones respectively.

The formation of iron-rich pyroxene skarn, was followed by a period of alteration and replacement of the pyroxenes by actinolite, calcite and quartz. Pyrrhotite, chalcopyrite and gold-bearing mineralization occur exclusively in the iron-rich skarn. A final stage of limonitic alteration affected the Inner Zone on Mini-Grid alone.

The mineralogy and chemistry of the barren and mineralized skarns were characterized by the study of thin sections, and by the analysis of representative samples using the electron-microprobe.

4.1.1 ANALYTICAL TECHNIQUES

An automated ARL-SEMQ electron-microprobe, fitted with an ORTEC energy dispersive spectrometer, was used for most silicate analyses. An accelerating potential of 10KeV and a probe current of 43nA was used. The wavelength dispersive method was used in the analyses of bismuth minerals, scheelite and some sulphides, due to the overlap between peaks.

The FORTRAN IV program EDATA2 (Smith and Gold, 1979) was used to process both energy dispersive and wavelength dispersive data. The detection limits of the SEMQ are 0.05wt% and 0.01wt% for energy dispersive and wavelength dispersive methods respectively. The full microprobe analyses of the silicate phases are given in Appendix T.

4.2 STAGES OF SKARN DEVELOPMENT

4.2.1 CONTACT METAMORPHISM

The Tahkandit Limestone is a siliceous, calcareous unit in which little dolomite has been recognised. Contact metamorphism during the intrusion of the Mount Brenner Stock has resulted in the formation of wollastonite and pyroxene-bearing marbles. The absence of clinopyroxenes more magnesian than Di_{26} reflects the lack of dolomite in the unmetamorphosed limestones.

Small, green garnets, containing up to 11wt% Cr_2O_3 and 6wt% V_2O_5 (Appendix 1, G3-7) are frequently overgrown by low-iron grossular garnet in the thermally metamorphosed basal pebble conglomerates.

4.2.2 BARREN WOLLASTONITE-BEARING SKARN

Wollastonite-bearing, calc-silicate rocks that are identified as skarn may be distinguished from wollastonite-bearing marbles by the presence of more iron-rich pyroxenes and by the complex replacement relationships between mineral phases.

Wollastonite-bearing skarn occurs in three locations. In Mini-Grid, the outer zone of unmineralized skarn is characterized by the lack of quartz, and the presence of wollastonite with minor grossular, idocrase and anorthite. In Mineral Gully, no equivalent outer zone exists between the mineralized skarn and the marbles; however, coarse wollastonite-anorthite skarn is developed in a thin horizon of banded skarn above Mineral Gully (Fig. 4.1). A thin horizon of barren, garnet-rich skarn was intersected in DDH-37, close to the margin of the main body of the Mount Brenner Stock.

1. THE OUTER ZONE, MINI-GRID

An outer zone of barren, wollastonite-bearing skarn (Plate 3b) is inferred from an intersection in DDH-27. The only quartz present is in corroded quartz pebbles in the more conglomeratic horizons. Pyroxene analyses indicate silica-deficient compositions, in which aluminum occupies both tetrahedral and octahedral sites. Minor idocrase, zeolites and prehnite are the only hydrous phases.

The quartz hornfels immediately underlying the Tahkandit Limestone is apparently unaffected by the skarn. Mineralogical changes parallel to the contacts of small monzonite

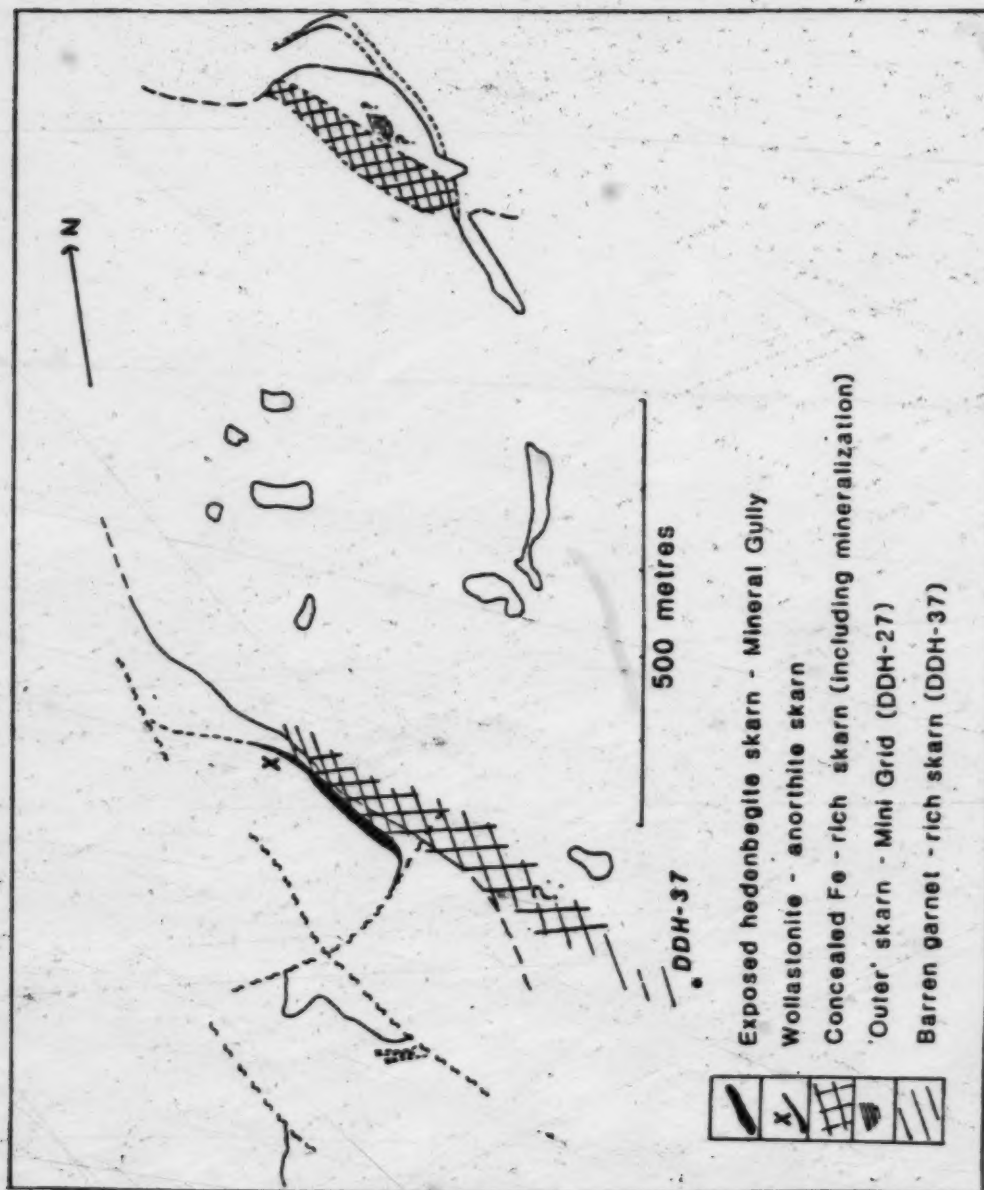
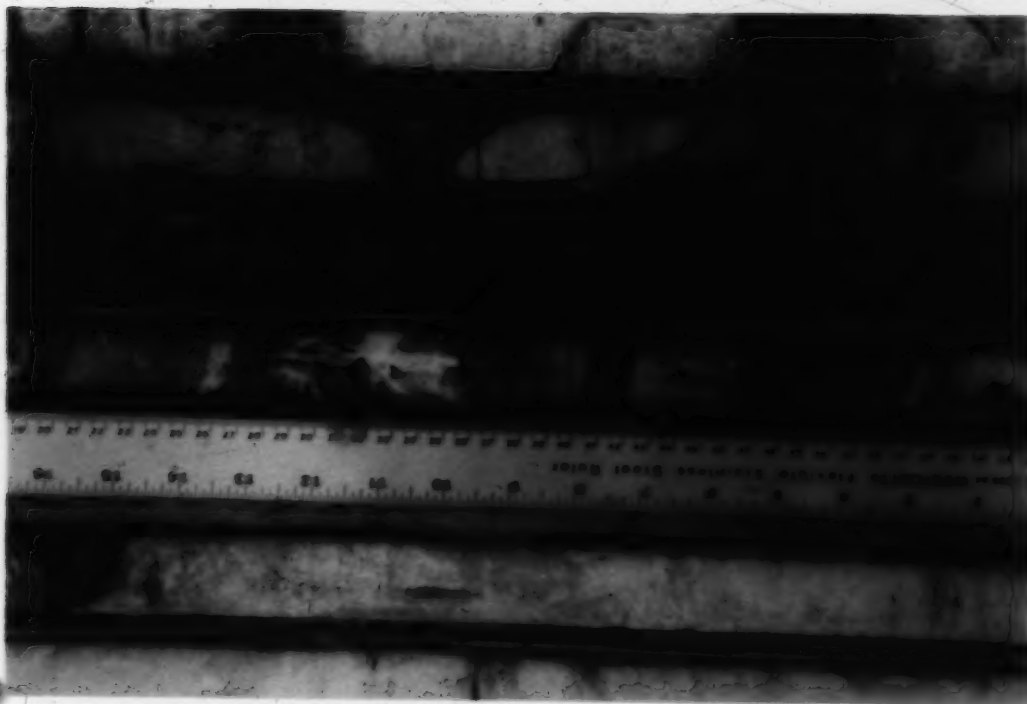


Figure 4.1. Location of the five main skarn types in the Mini-Grid and Mineral Gully areas.

PLATE 3

PLATE 3a. Drill core from the garnet-rich skarn of DDH-37, showing a finely developed banding between the garnet and pyroxene.

PLATE 3b. Drill core showing part of the wollastonite-bearing skarn of DDH-27 ('Outer skarn' of Mini-Grid). Typical unaltered monzonite is seen in the centre of the field of view.



COLOURED PICTURES
Images en couleur

sills, suggest some degree of control by the intrusive; however, mineral banding is weakly developed and rarely monomineralic. An example of a contact zone between the skarn and a small sill, is illustrated in Figure 4.2. Fine-grained wollastonite, anorthite and pyroxene replace the dioritic sill along a narrow contact zone. The presence of relict igneous pyroxenes within wollastonite-bearing skarn suggests a partial assimilation of the intrusive forming a narrow zone of endoskarn. A weak zoning is developed parallel to the contact, and includes a thin monomineralic layer of pyroxene separating the wollastonite-anorthite zone from a pyroxene (Hd_{32-36})-grossular assemblage. This relationship suggests a movement of components downwards, as wollastonite within the grossular-bearing horizon becomes progressively more altered upwards. Aluminous pyroxenes associated with the wollastonite-anorthite assemblage would have formed earlier than the low aluminum pyroxenes coexisting with the garnet.

A complex paragenesis is observed in samples containing garnet and idocrase (Fig. 4.4). Wollastonite is always the earliest mineral formed, often coexisting with pyroxene, but locally replaced by it. Idocrase, where present, replaces both wollastonite and pyroxene (Plate 4). Grossular-rich garnet (Gr_{75-85}) replaces all these minerals, followed by more anisotropic and iron-rich, vug-filling garnet. Rare prehnite replaces wollastonite, while zeolites form late veinlets.

In a single sample, two distinct pyroxene compositions can be distinguished on the basis of their aluminum content. (Fig. 4.3b). Aluminous pyroxenes (Appendix 1, Table 2.) in which up to 11% of the tetrahedral sites are occupied by aluminum, coexist with either anorthite or idocrase. There is a decrease in aluminum content towards the grain boundaries of both the high and low Al pyroxenes, suggesting at least a partially contemporaneous formation. There is no evidence for the replacement of one type of pyroxene by the other.

2. WOLLASTONITE-ANORTHITE SKARN, MINERAL GULLY

A layered, wollastonite - anorthite and pyroxene skarn, located a short distance from the main outcrops of Mineral Gully, (Fig 4. 1), contains an early assemblage of coarse-grained wollastonite and anorthite (Plate 5a). Reaction between these two, minerals has produced rims of grossular garnet(Gr_{79}) at some of the mutual grain boundaries. Aluminous sphene is a common minor phase. The paragenetic relationships are represented

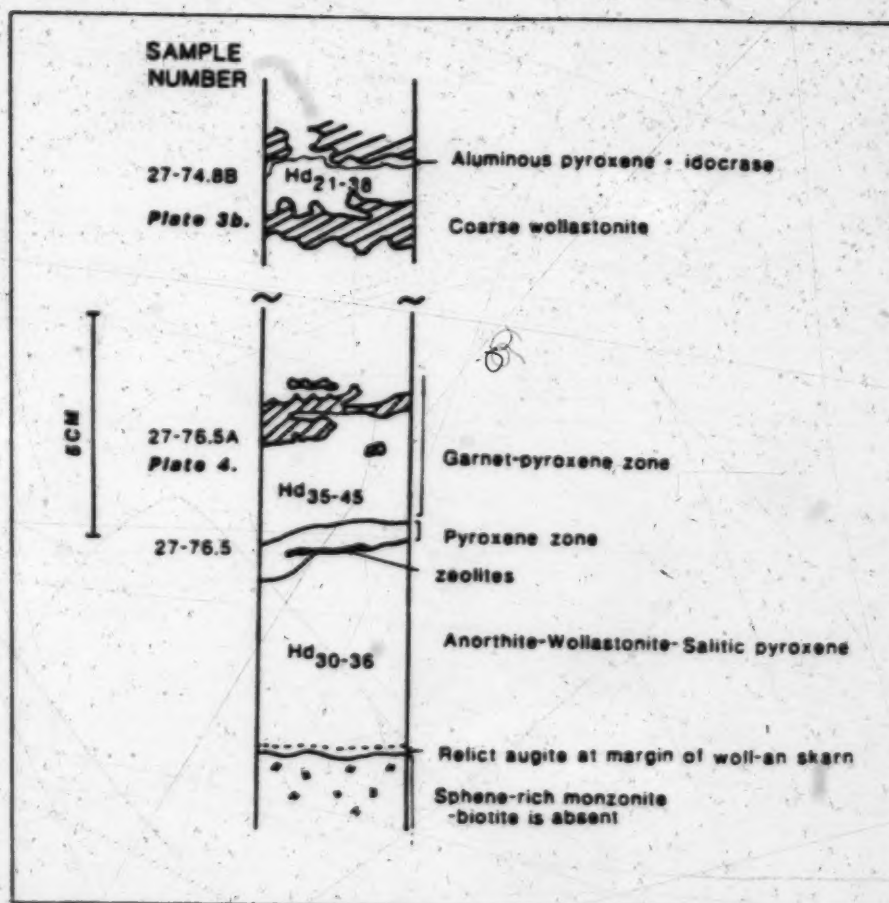


Figure 4.2. Details of a contact zone between the barren wollastonite-bearing skarn of DDH-27 and a slightly altered monzonite sill.

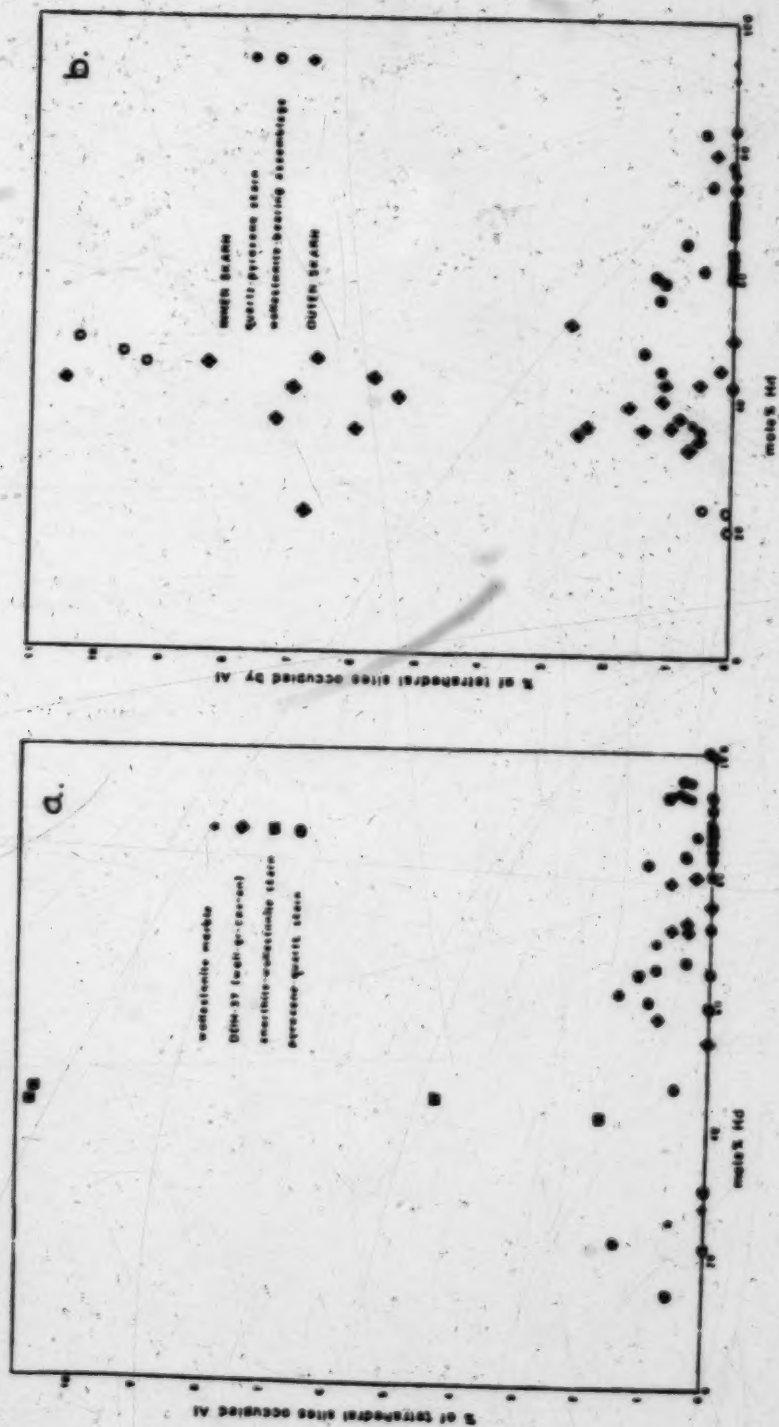


Figure 4.3. Variations in aluminum and iron contents of pyroxenes from a) Mineral Gully and b) Mini-Grid showing the range of Al substitution in the tetrahedral sites.

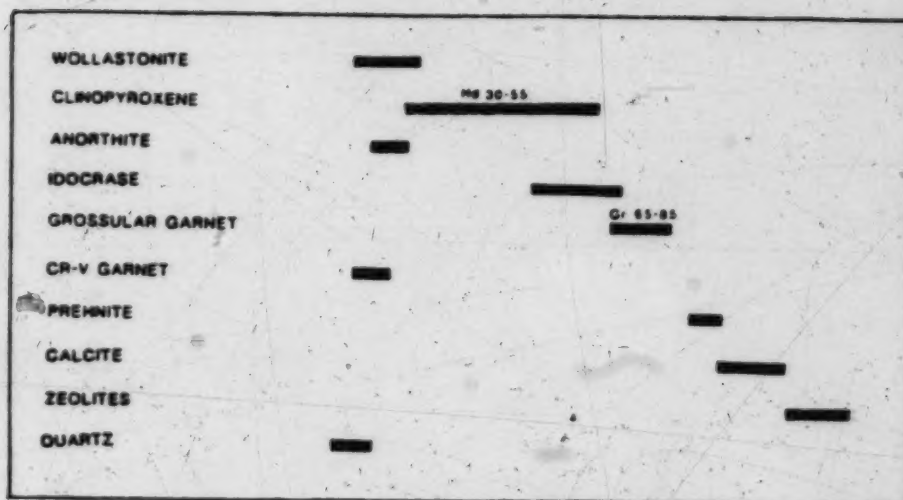
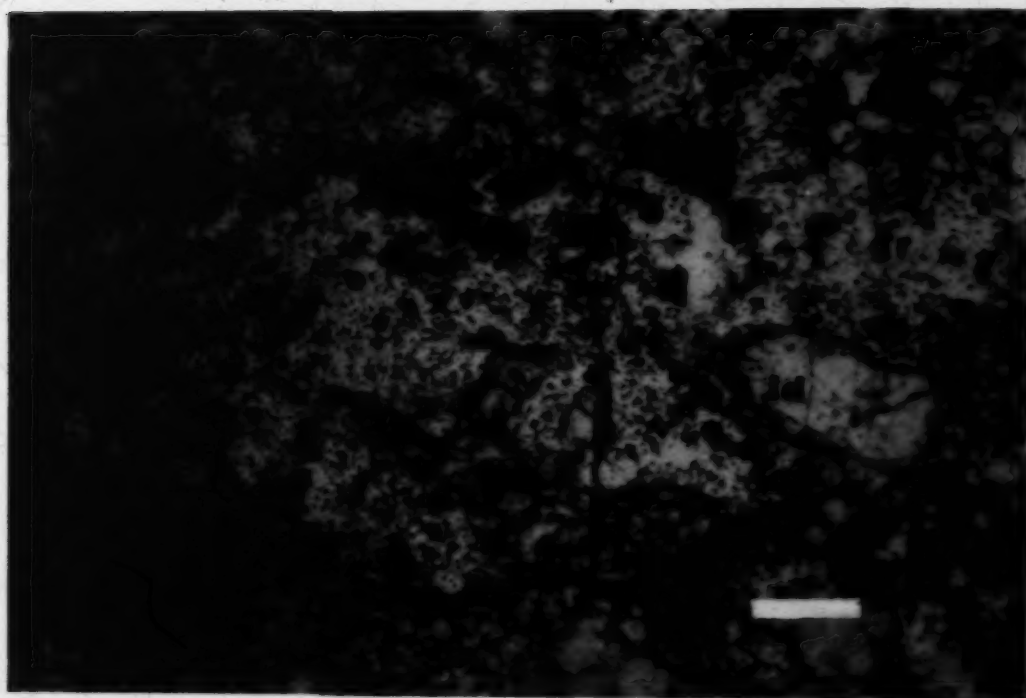
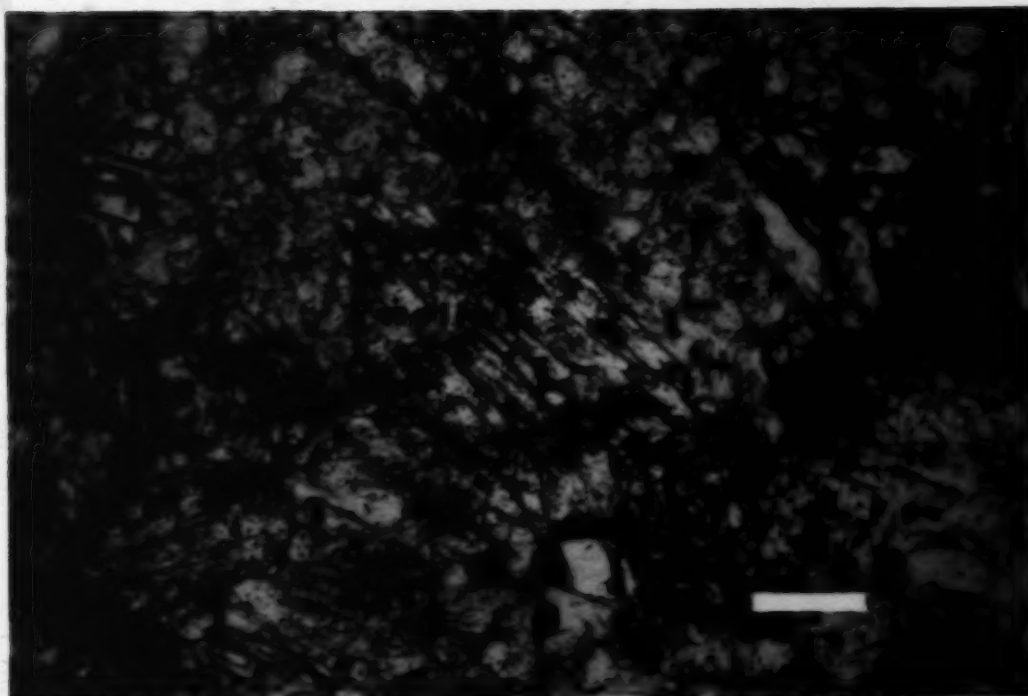


Figure 4.4. Paragenesis of skarn silicates in the 'Outer Zone' (DDH-27) of Mini-Grid.

PLATE 4

PLATE 4. Replacement textures between wollastonite (woil), pyroxene, idocrase (id), and garnet (gr) from DDH-27. (Bar=0.4mm.)



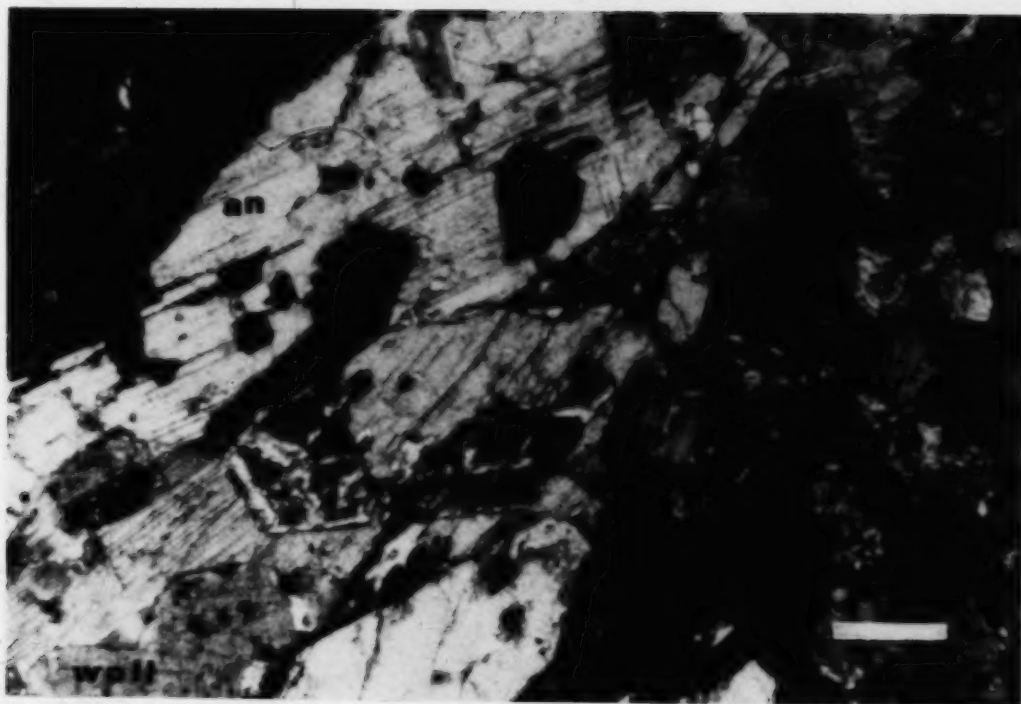
COLOURED PICTURES
Images en couleur

PLATE 5

PLATE 5a. Anorthite (an) and wollastonite (wo) skarn from Mineral Gully.

(Bar=0.4mm.)

PLATE 5b. Garnet-rich skarn from DDH-37, showing the overgrowth of colourless and euhedral grossular by pinker and more iron-rich garnet. (Bar=0.4mm.)



in Figure 4.5b.

Pyroxenes maintain a constant $\text{Fe}/(\text{Fe}+\text{Mg}+\text{Mn})$ ratio, however there are two distinctly different compositional types (Fig. 4.3b). Low Al pyroxenes are common in the wollastonite-rich and pyroxene-rich layers. Dark, olive-green pyroxenes, containing as much as 1.4wt% TiO_2 and 7.0wt% Al_2O_3 (Appendix 1, P108) are present only in the pyroxene-rich layers, and replace the low Al pyroxenes.

Red idocrase may completely replace pyroxenes; however, it is sparsely developed, and does not occur elsewhere on the south side of the sill.

3. GROSSULAR-WOLLASTONITE-HEDENBERGITE SKARN (DDH-37)

The mineralogy and paragenesis (Fig. 4.5a) of the garnet-rich skarn (Plate 3a) intersected in DDH-37 is simple. Garnet is virtually absent from the upper 30cm and lower ~~metre~~ of the horizon. At the upper contact, fine pyroxene is developed immediately adjacent to the intrusive. This upper zone is characterized by very fine banding which is caused by regular variations in grain-size of the pyroxenes. Sphene, plagioclase and quartz make up the remainder of the assemblage. The sub-calcic augites of the intrusive, are replaced by salite and ultimately by ferruginous salites (Hd_{60-80}), which are typical of most of the skarn. The compositional variations among the pyroxenes are illustrated in Figure 4.8. Calcic pyroxene is accompanied by anorthite in the contact region, rather than igneous andesine. Fine-grained wollastonite and anorthite are the earliest formed minerals, while clinopyroxene replaces wollastonite at the grain boundaries. Pale, euhedral, grossular-rich garnet (Andr_{16}) are commonly overgrown by pinker and more iron-rich (Andr_{33}) garnet (Plate 5b). Quartz and calcite are rare or absent. Calcite and scapolite form small, widely-spaced veins. Fine-grained sphene forms small, cross-cutting zones that bear no relation to other veins.

At the lower contact of the skarn, a thin horizon of chlorite and pyrrhotite separates fine-grained, anorthite-pyroxene skarn from slightly altered intrusive.

The mineral assemblages of this skarn may be explained by a reaction metasomatism between the monzonite supplying aluminum and iron and the limestone. Wollastonite began to form during the contact metamorphic event, continuing to develop during skarn formation by the metasomatic redistribution of silica. The most aluminous phase, anorthite, is concentrated at the upper and lower margins of the skarn horizon,



Figure 4.5. a) Paragenesis of silicates in the barren garnet-rich intersection of DDH-37.

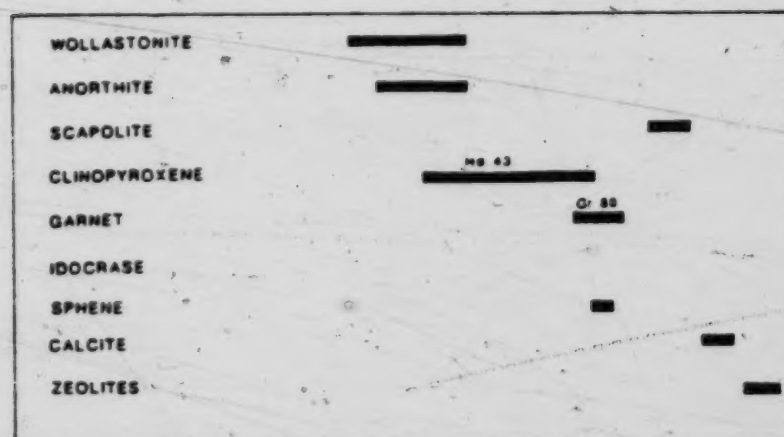


Figure 4.5. b) Paragenesis of the barren wollastonite-anorthite skarn from the upper region of Mineral Gully.

closest to the inferred source of aluminum.

4.2.3 IRON-RICH, PYROXENE SKARN

Iron-rich pyroxene skarn is the most important skarn-type both by volume and by being the main host of mineralization. Small differences in chemistry, textures and mineralogy distinguish the iron-rich skarns of the Mineral Gully and Mini-Grid areas.

Massive, green pyroxene skarn replaces both the Tahkandit Limestone and the top of the Devonian-Mississippian formation in the northern area. The pyroxene that forms the bulk of this skarn varies in composition both within and between grains from Hd_{62} to Hd_{11} (Fig 4.8c). The massive skarn of Mineral Gully is similar in many respects to that of Mini-Grid; however, the pyroxenes are more ferruginous, with a range from Hd_{88} to Hd_{100} . These hedenbergitic pyroxenes show very slight but detectable zoning towards both iron-rich and magnesium-rich rims; however, total variations within single grains are typically in the order of only 2.5 wt% Fe.

Evidence that an earlier diopsidic pyroxene assemblage was present earlier than the iron-rich skarn, is found in a sample of float found below Mineral Gully. Colourless diopside (Di_{94}) cores (Appendix 1, P101) are overgrown by green hedenbergite (Hd_{88-11}). The overgrowth of hedenbergite is sharp (Plate 6b), suggesting that the increasing iron content of the pyroxene was not a gradual process.

Garnet does not occur in the iron-rich skarn of Mini-Grid; however two occurrences are recorded in Mineral Gully. Iron-rich grossular (Gr_{63}) occurs locally as an interstitial phase in hedenbergitic skarn, replacing pyroxenes along grain boundaries (Plate 7a). Andradite ($Andr_{95}$) was found in the same sample of float described above, in which coarse and finely zoned andradite replaces hedenbergitic pyroxene (Hd_{85}). The garnet itself is highly fractured and replaced by calcite and pure hedenbergite (Hd_{100}) (Plate 6b).

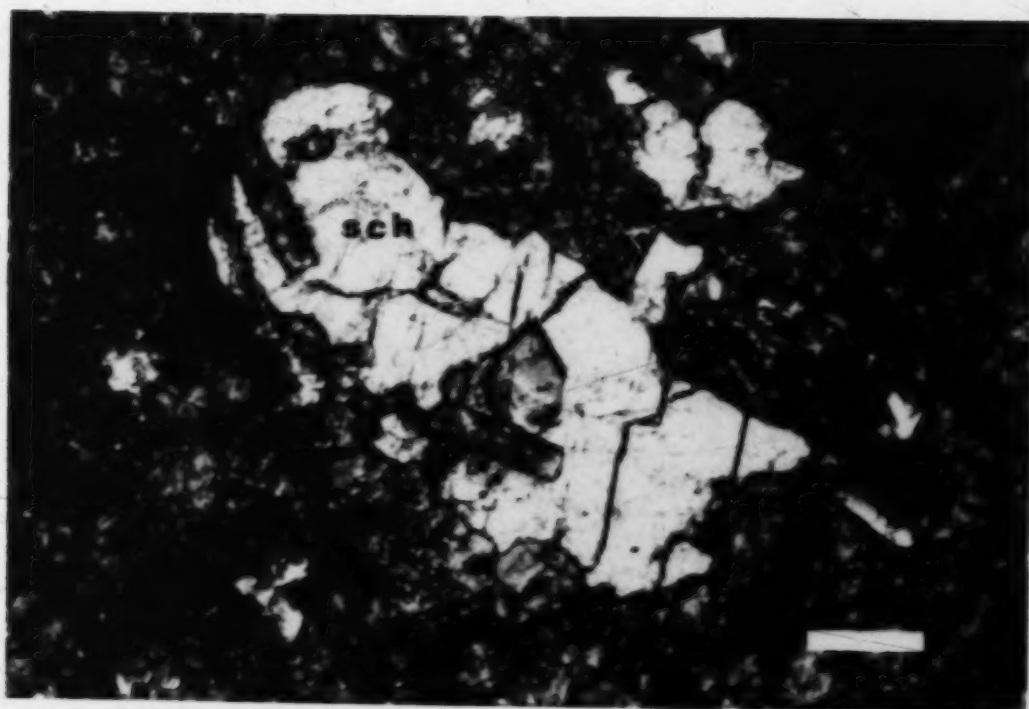
In detail, the textures, mineralogy and paragenesis of the two iron-rich skarns are similar (Figs. 4.6, 4.7). Plate 8 illustrates textures in the pyroxene skarn of Mini-Grid. It is common to see large, broken and radiating pyroxene grains replaced by later actinolite, calcite and quartz. The euhedral growth of pyroxene into quartz and calcite-filled vugs (Plate 8a) indicates that these were open spaces at the end of this stage of skarn

3

PLATE 6

PLATE 6a. Coarse-grained scheelite in hedenbergitic skarn from Mineral Gully.
(Bar=0.4mm.)

PLATE 6b. Andradite-bearing float from below Mineral Gully.
di=diopside, sal=salite, hd=hedenbergite, andr=andradite, cal=calcite. (Bar=0.2mm.)



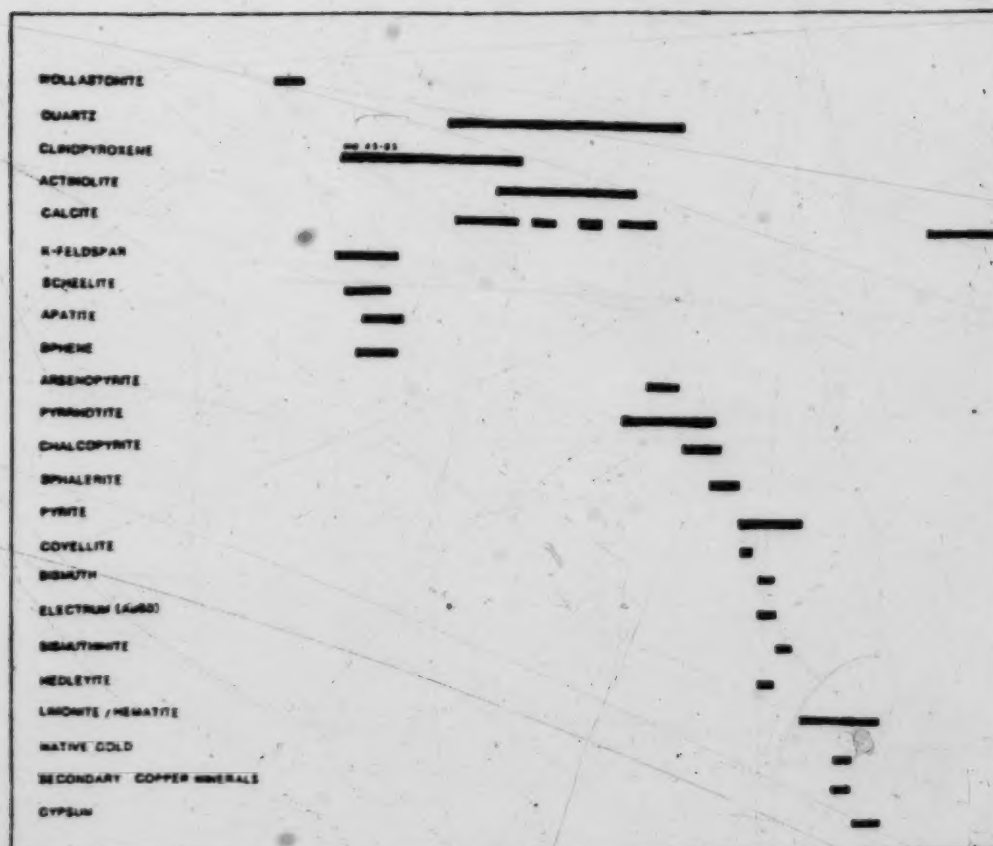


Figure 4.6. Detailed paragenesis of the five stages of skarn formation recognised in the iron-rich skarn of Mini-Grid.

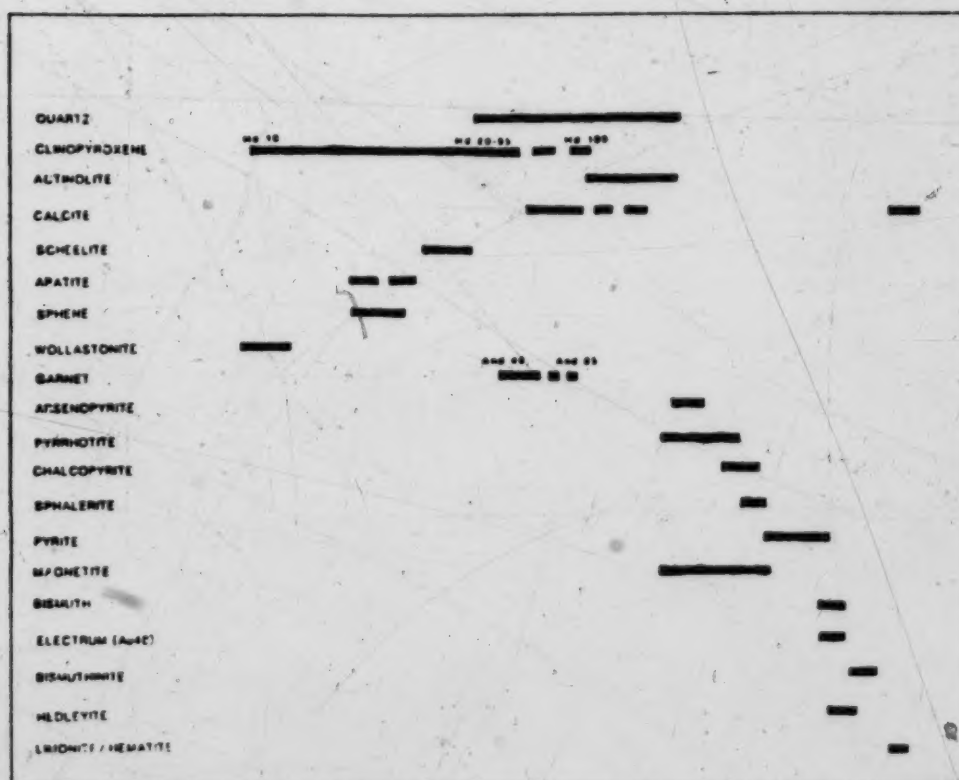


Figure 4.7. Detailed paragenesis of the hedenbergitic skarn in Mineral Gully.

PLATE 7

PLATE 7a. Iron-rich grossular in hedenbergitic skarn, Mineral Gully. (Bar=0.1mm.)

PLATE 7b. Contact of iron-rich pyroxene skarn with monzonite. (Bar=0.4mm.)

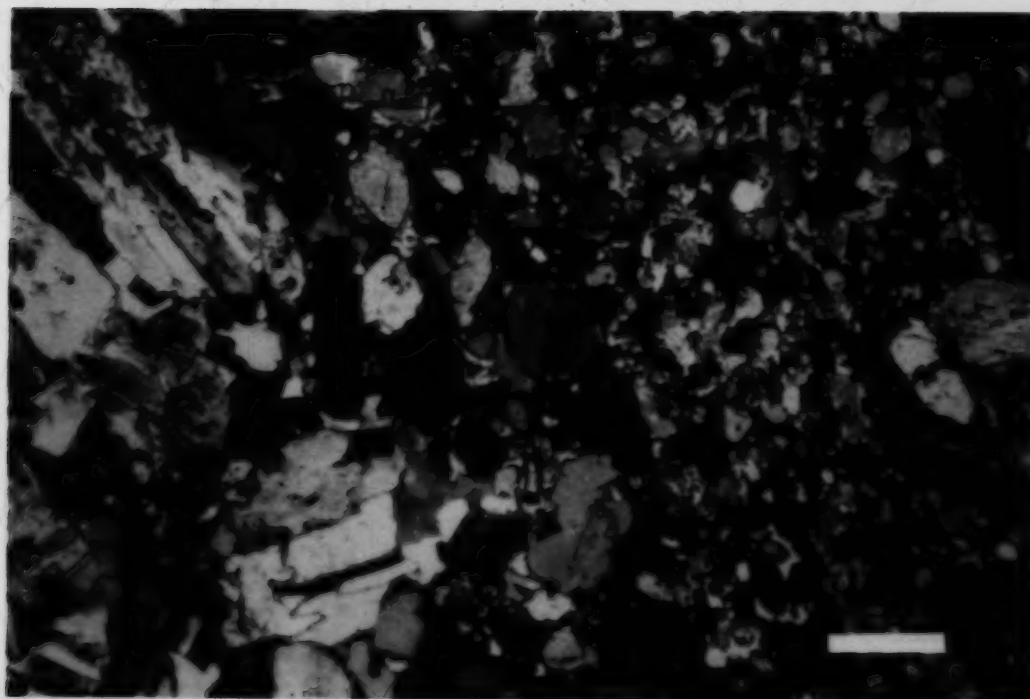
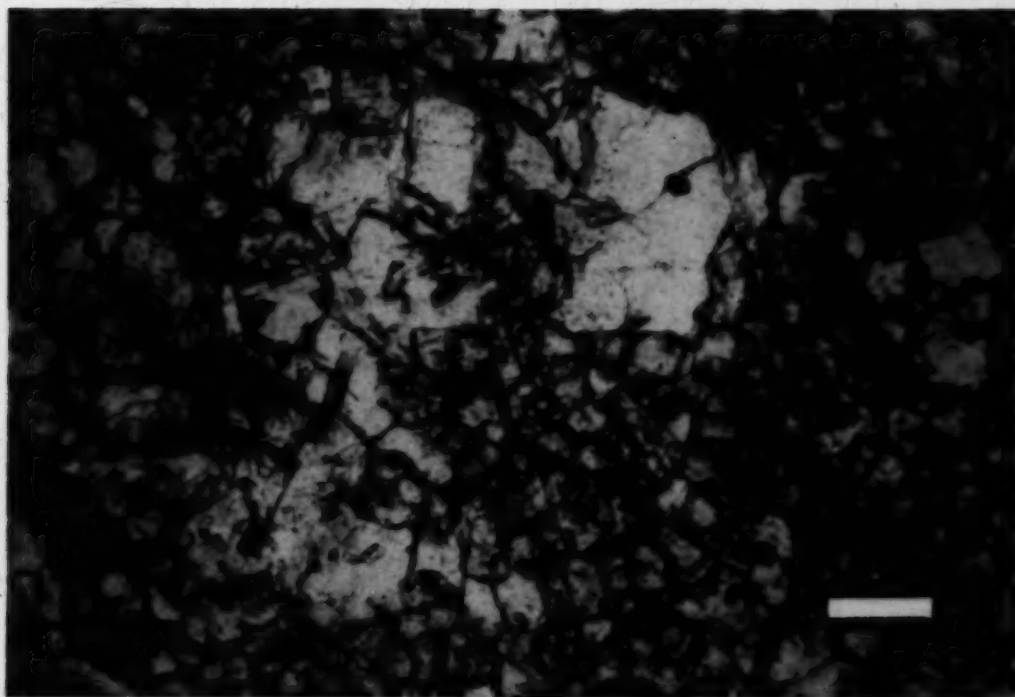
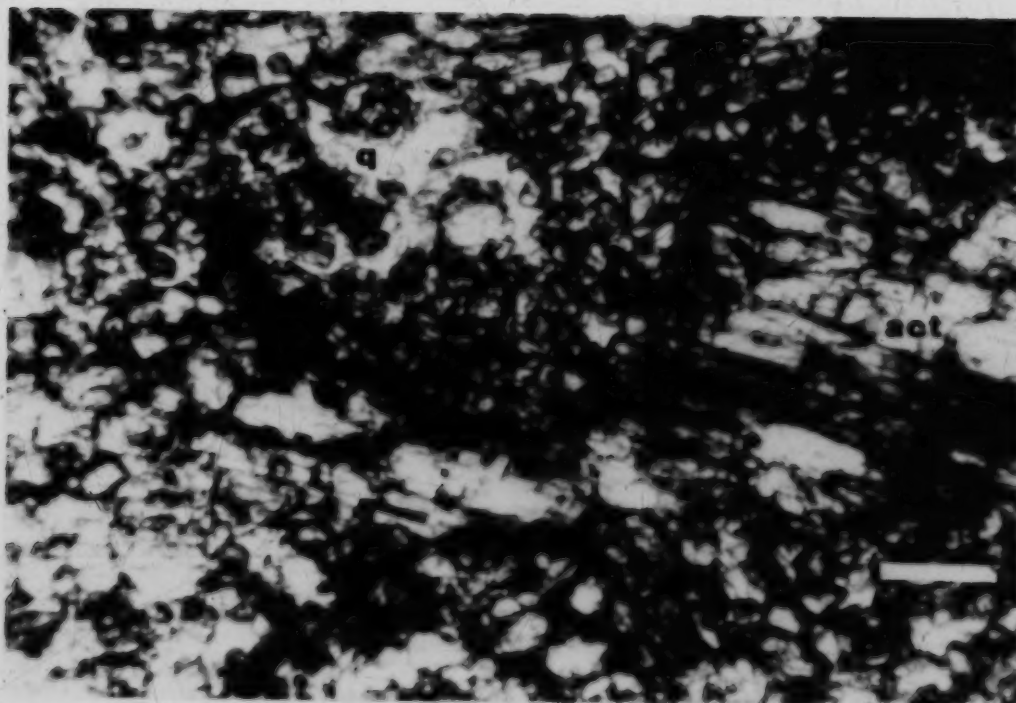
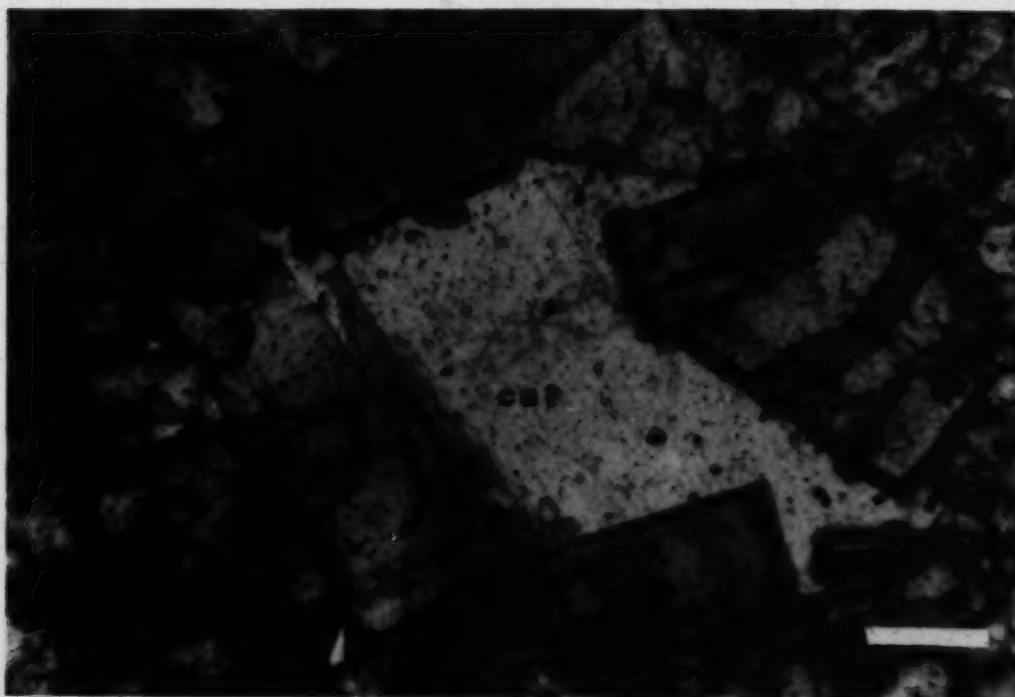


PLATE 8

PLATE 8a. Open-space filling by calcite in skarn from Mini-Grid. (Bar=0.1mm.)

PLATE 8b. Fine-grained pyroxene skarn replaced by coarser-grained actinolite (act) and quartz (q). (Bar=0.1mm.)



formation. Large, subhedral scheelite grains (Plate 6a), containing less than 0.2 wt% Mo, formed during the pyroxene skarn stage. Some scheelite forming cross-cutting veins probably represent redeposition of primary scheelite by later fluids. K-feldspar is the only important aluminous mineral and is present only in skarn formed from the Devonian-Mississippian protolith. With this minor exception, the skarn formed from the quartz-rich hornfels is identical to that in the Tahkandit Limestone.

In Mineral Gully, pyroxene accounts for over 80% of the rocks by volume, compared to only 60% in Mini-Grid. The smaller amount of open vug space remaining after this early skarn stage would have had an important effect on determining the permeability of the rock to later mineralizing fluids.

The sharp contact between skarn and wollastonite-bearing marbles is well exposed in Mineral Gully. Plate 9a, illustrates the effect of the encroaching skarn front on the marbles. The field of view shows a sharp boundary between an area of fine-grained calcite with corroded wollastonite and unaltered wollastonite marble. Wollastonite and hedenbergite occur as a stable assemblage in some of the skarn veinlets found beyond the main skarn front (Plate 9b).

Small zones and veins of pyroxene, sphene and feldspars form endoskarn within monzonite sills. Plate 7b, illustrates one of the few examples of the contact between iron-rich skarn and monzonite. Biotite is absent from the intrusive immediately adjacent to the skarn, but otherwise the monzonite is unaltered. The pyroxenes in these zones are often more aluminous (Appendix 1, P1-P6) than those in the main skarn. Alteration veins in the intrusive may also contain actinolite, molybdenite, calcite and quartz.

The iron-rich pyroxene skarn in both areas was replaced by an assemblage of actinolite, calcite and quartz during a period of retrograde alteration. The degree of this alteration is considerably greater in the northern skarn body, reflecting the greater degree of permeability over that to the south.

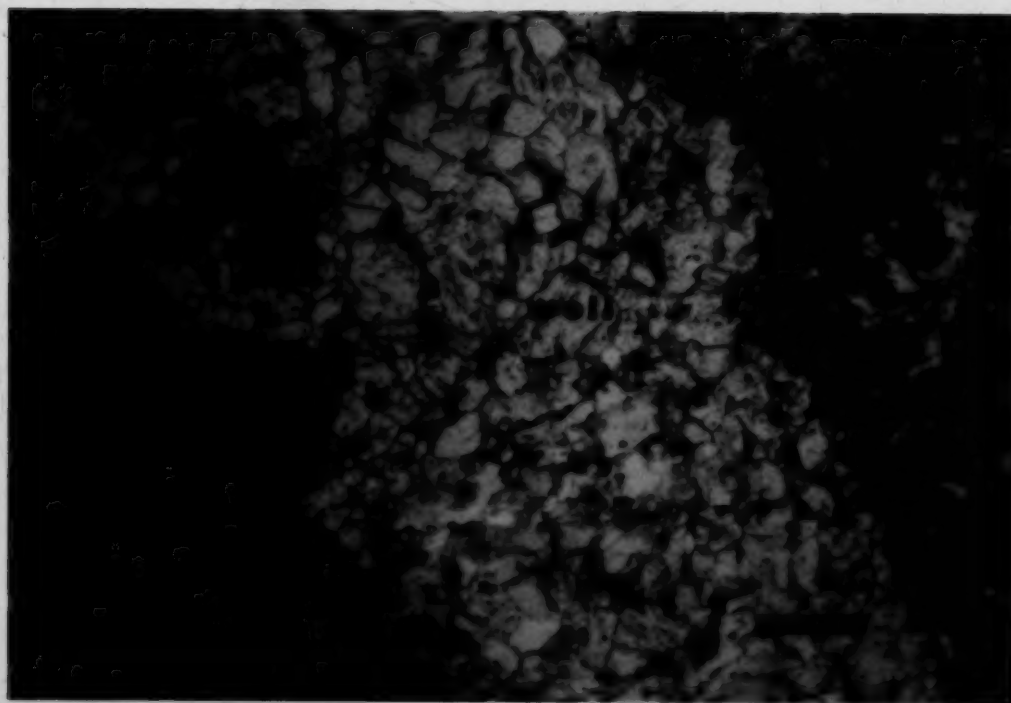
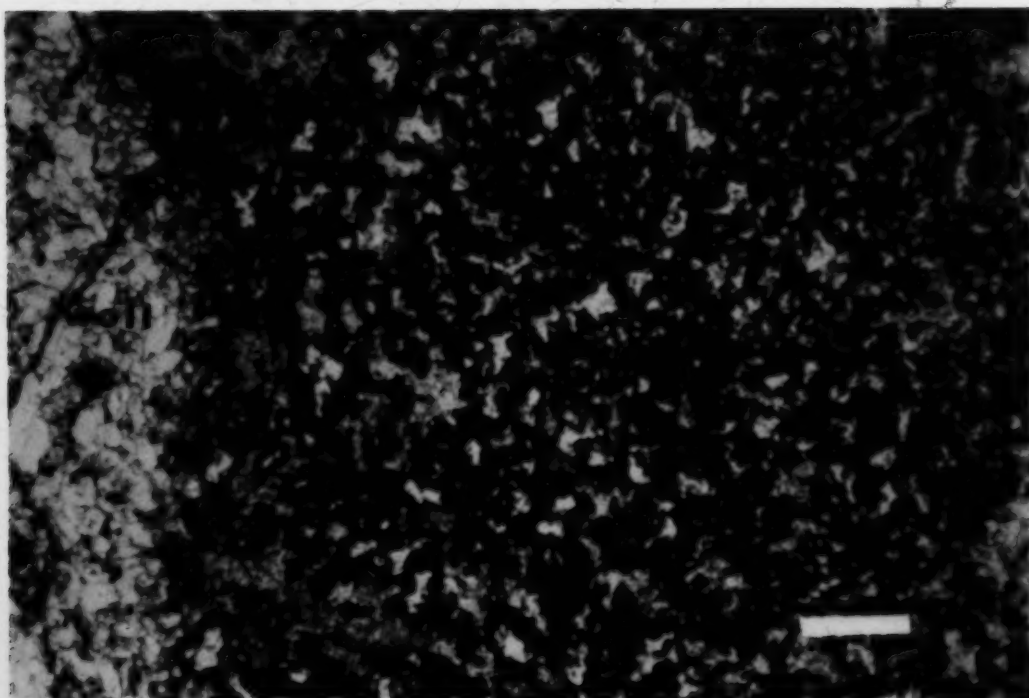
4.2.4 MINERALIZATION

The main period of mineralization followed the deposition of skarn silicates. Spatially, sulphide mineralization extends beyond the earlier skarn, to form veinlets in the adjacent intrusives and quartz hornfels. There is often a spatial association between

PLATE 9

PLATE 9a. Part of the calcite-rich contact zone between wollastonite-bearing marble (woll) and hedenbergite skarn in Mineral Gully. (Bar=0.4mm.).

PLATE 9b. Coexisting wollastonite and hedenbergite in skarn from Mineral Gully.
(Bar=0.4mm.)



actinolite and the sulphides (Plate 10), suggesting that both formed either from the same cooling fluid, or from fluid that followed similar pathways. However, replacement textures indicate that most actinolite formed before the mineralizing event.

Pyrrhotite forms more than 70% of the total sulphides, but is less abundant in Mineral Gully. Magnetite is locally important in the skarn on the southern margin of the sill, where it occupies a position early in the paragenesis of the opaque mineral assemblage (Plate 11); however, it has not been recognised in Mini-Grid. Massive magnetite replaces chalcopyrite and pyrrhotite-bearing skarn in samples of float from below Mineral Gully. The source of this material is unknown. Sphalerite, arsenopyrite, pyrite, cubanite, pentlandite and covellite are locally developed in both skarns. The assemblage of electrum and bismuth minerals represents less than 1% of any sample in which it is present.

SULPHIDES

Two textural styles of sulphide mineralization are represented by the replacement of skarn silicates and veining. Plate 10 shows the replacement of pyroxene and amphibole by pyrrhotite and chalcopyrite. There are no other minerals produced by this reaction. Sulphide veinlets are less common, but make up most of the mineralization in the partially skarnified quartzites and intrusives.

Pyrrhotite and arsenopyrite are the earliest formed sulphides. The latter is rare, but forms euhedral grains adjacent to, or within pyrrhotite. Chalcopyrite is more abundant at the margins of pyrrhotite aggregates and veinlets. Numerous sphalerite blebs and stars in chalcopyrite suggest that both exsolution of sphalerite in chalcopyrite and replacement of chalcopyrite by sphalerite occurred. Cubanite exsolution lamellae in chalcopyrite are common, particularly in regions of the highest gold values. The lamellae are often replaced by pyrite, and less frequently by covellite (Plate 12a). The paragenetic position of molybdenite, which occurs in small amounts in the mineralized skarn, is uncertain; however, it clearly predates chalcopyrite (Plate 11b). Pyrite is not a primary mineral of the main sulphide stage. It occurs only as an alteration product of pyrrhotite or cubanite or in small veinlets in slightly skarnified hornfels adjacent to the main skarn horizon.

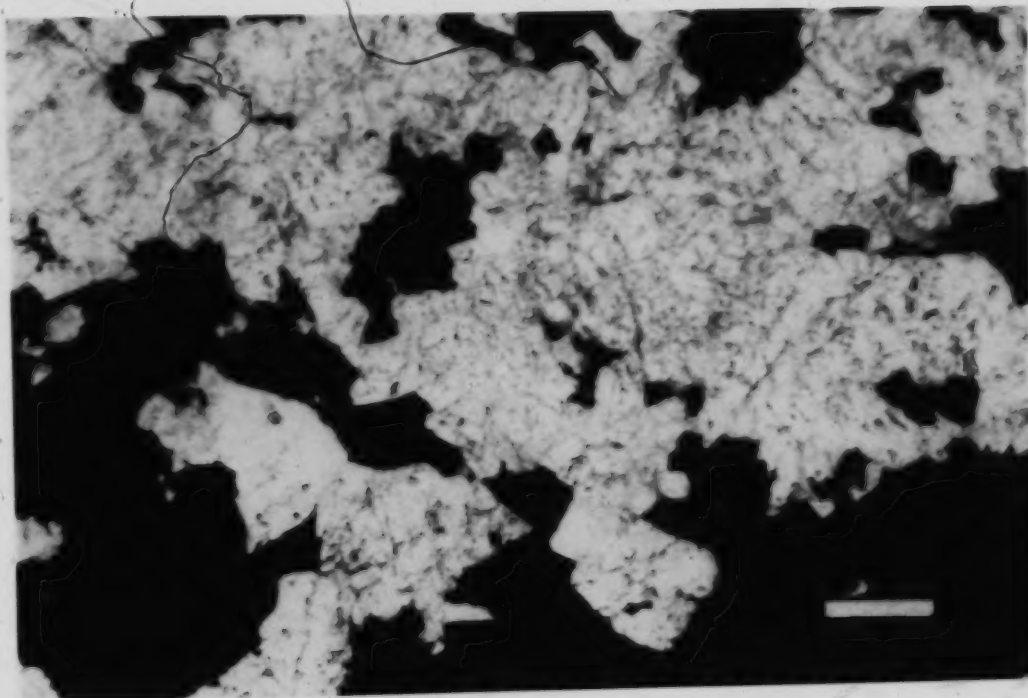
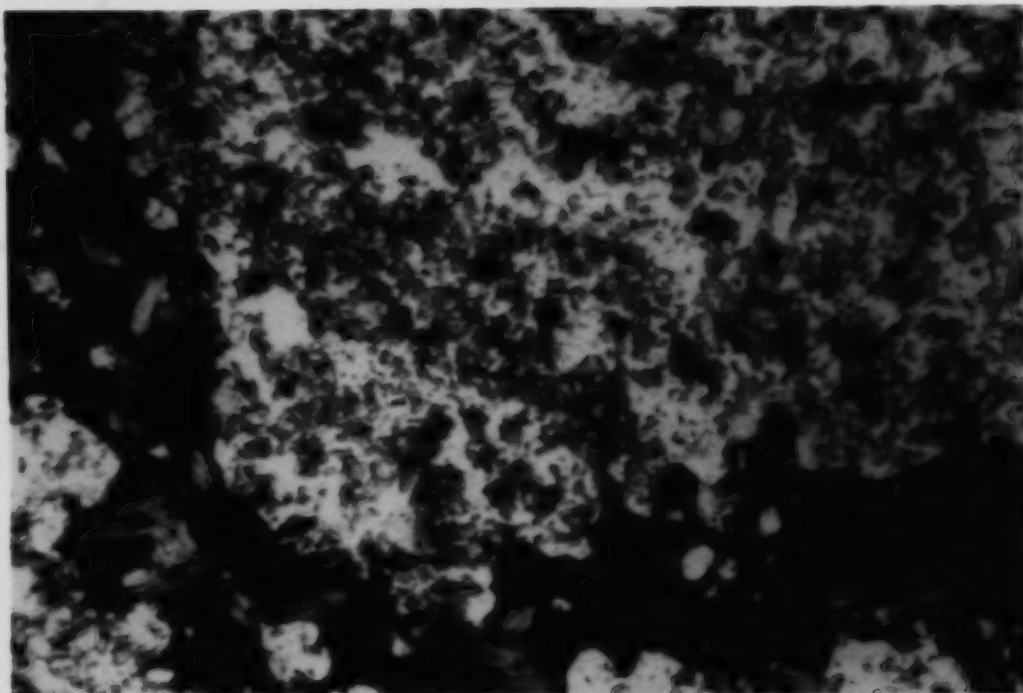
THE BISMUTH-ELECTRUM ASSEMBLAGE

An assemblage of electrum and bismuth minerals formed after the main episode of sulphide deposition. Native bismuth and a bismuth-tellurium mineral are the most abundant

PLATE 10

PLATE 10a. Sulphide and actinolite veining in fine-grained, quartz-rich skarn from Mini-Grid. (Bar=0.4mm.)

PLATE 10b. Replacement of pyroxene skarn by pyrrhotite and chalcopyrite, from Mini-Grid. (Bar=0.4mm.)

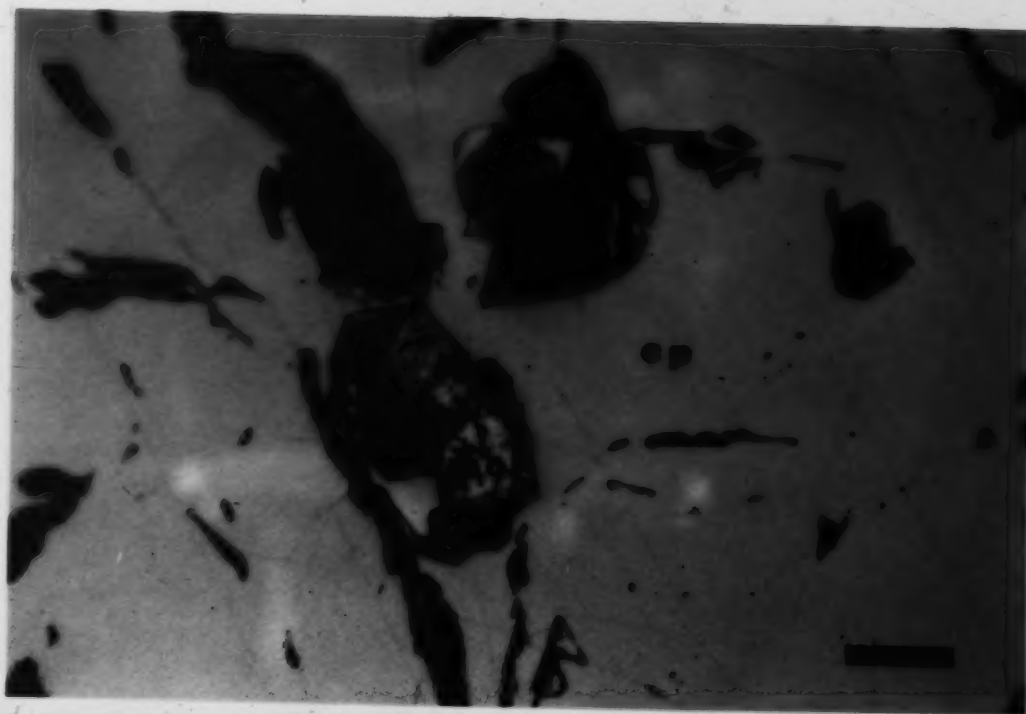
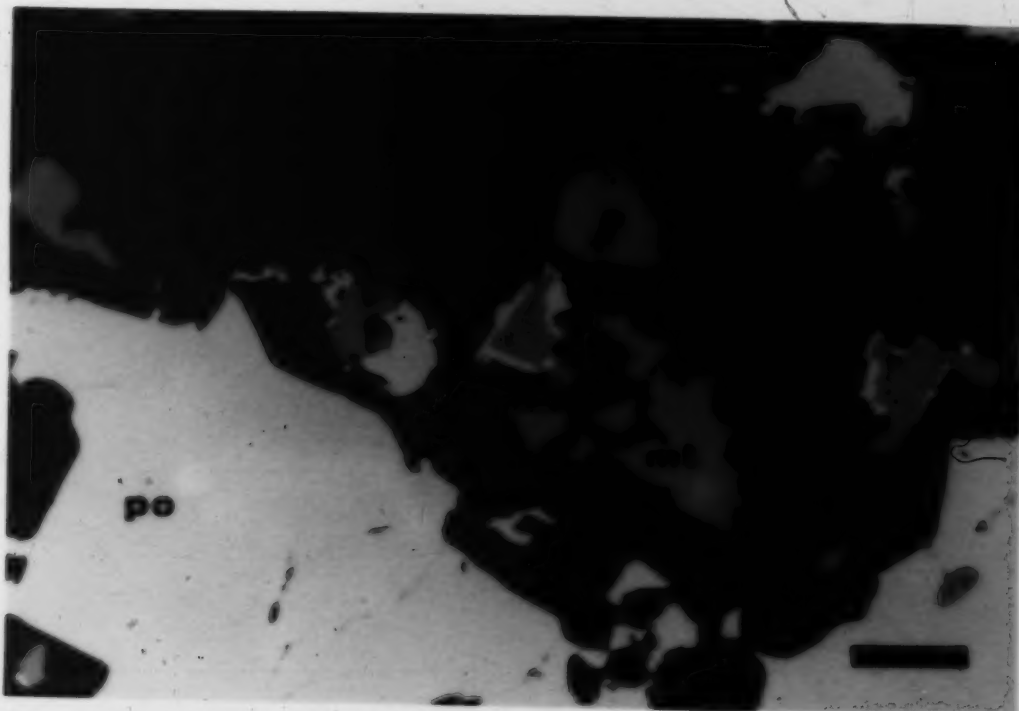


COLOURED PICTURES
Images en couleur

PLATE 11

PLATE 11a. Magnetite rimmed by later pyrrhotite. (Bar=0.05mm.)

PLATE 11b. Euhedral plates of molybdenum in chalcopyrite, from Mini-Grid.
(Bar=0.05mm.)

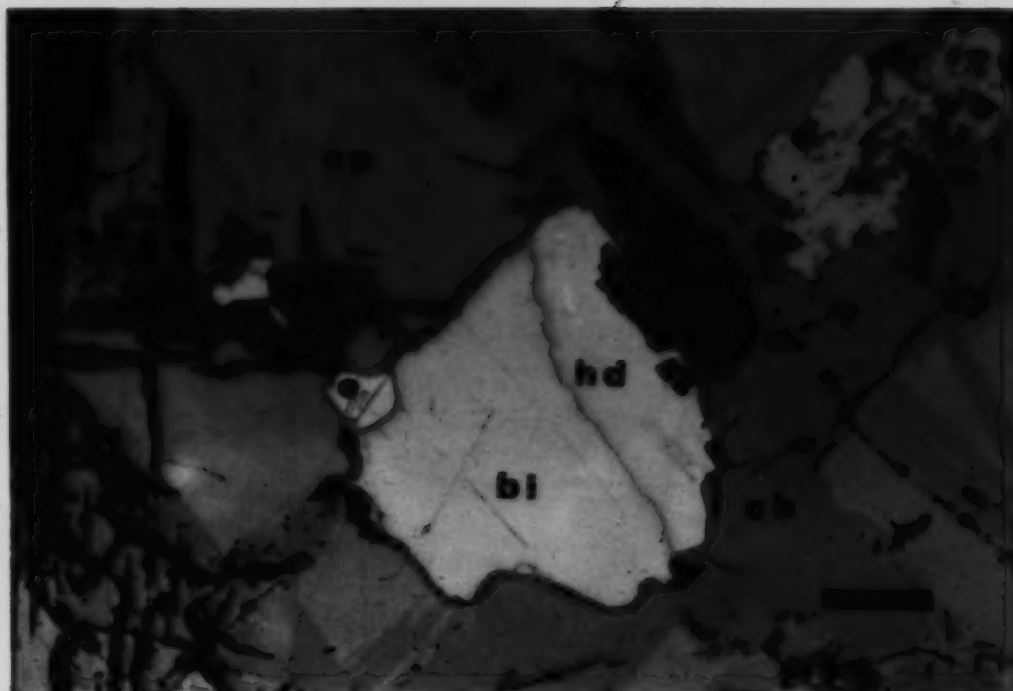
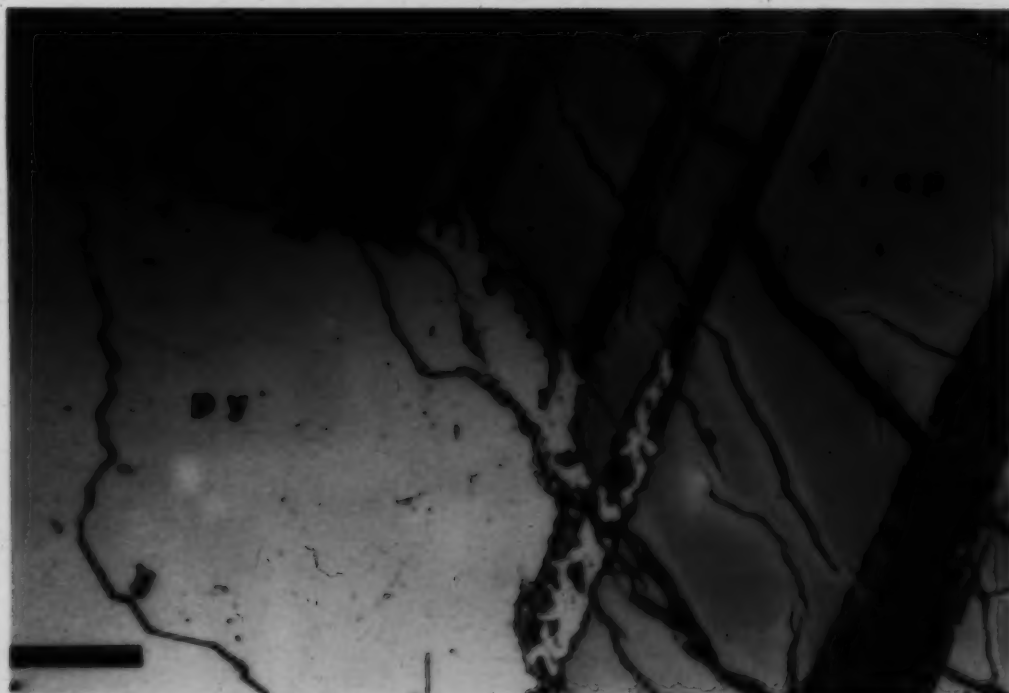


COLOURED PICTURES
Images en couleur

PLATE 12

PLATE 12a. Pyrite replacing covellite, which itself replaces cubanite lamellae in chalcopyrite. (Bar=0.05mm.)

PLATE 12b. Hedleyite (hd), bismuth and electrum crosscutting cubanite (cb) exsolution lamellae in chalcopyrite. (Bar=0.05mm.)



phases. The latter phase is a bluish-grey mineral with strong bireflectance and a strong blue to brown birefringence (Plate 12b). The formula, $\text{Bi}_{1.4}\text{Te}$ (Table 4.1), is higher in bismuth than any tellurium mineral recorded in the literature. The abundance of visible bismuth blebs within this phase suggests that very fine native bismuth, below the resolution of the microscope, may account for the high bismuth values. It is most likely that the mineral is hedleyite. The composition of hedleyite ($\text{Bi}_{1.4}\text{Te}$) itself is in some doubt. The published formula of the natural mineral is higher in bismuth than the synthetic material (Bi_2Te_3). It is suggested that this difference may also be due to contamination in the natural samples by native bismuth (Uytenbogaardt and Burke, 1971). A bismuth-sulphur telluride, which is virtually indistinguishable from the bismuth telluride (Plate 13a), is identified as Joseite-A ($\text{Bi}_{4.2}\text{Te}_{1.2}\text{S}$). The composition (Table 4.2) is again higher in bismuth than those published, suggesting that submicroscopic bismuth or bismuthinite may be present. Bismuthinite commonly replaces bismuth (Plate 13b). Hessite (Ag_2Te) was only observed as very small lamellae in bismuth.

Electrum is the only gold mineral in the bismuth-bearing assemblage. The gold content of the electrum is higher in Mini-Grid ($\text{Au}_{77.65}$) than in Mineral Gully (Au_{80}). Blebs and veinlets of electrum and bismuth minerals are located at the margins of chalcopyrite aggregates and veinlets, but rarely occur within pyrrhotite. The relationship to the silicate gangue is similar to that of chalcopyrite, in that there is a tendency for bismuth in particular, to follow cleavages and grain boundaries of gangue minerals (Plate 14a). Electrum, bismuth and hedleyite veinlets occur in fractures in the sulphides. One such mineralized fracture, seen in Plate 14b, offsets the cubanite lamellae in chalcopyrite. Electrum and bismuth minerals are often spatially associated with arsenopyrite (Plate 15a); however clear exsolution textures are rare (Plate 15b).

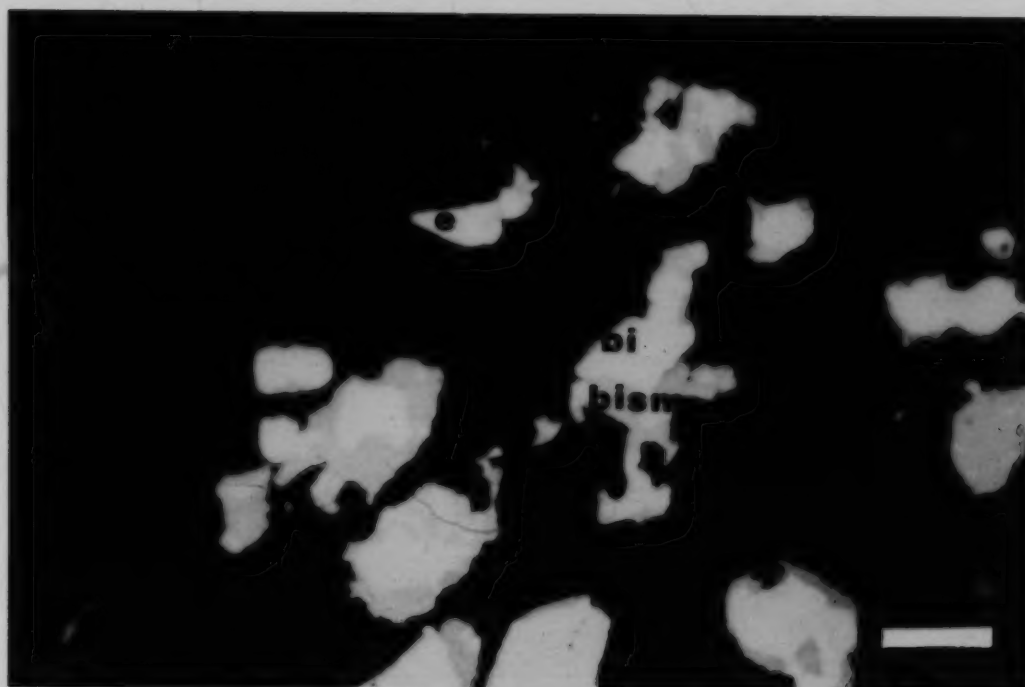
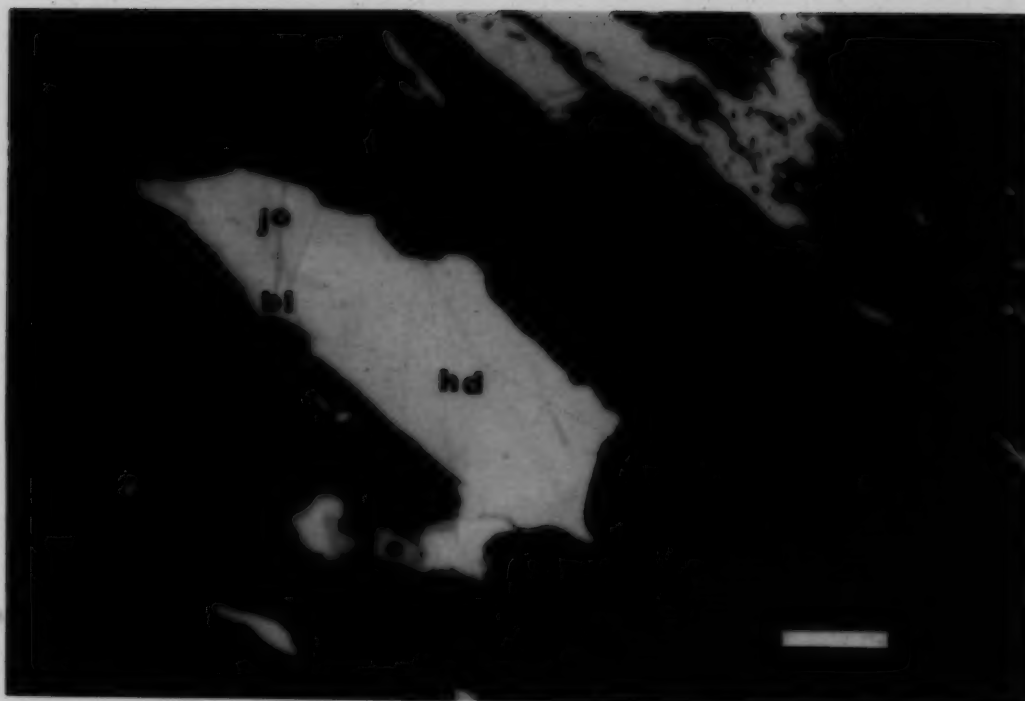
4.2.5 LATE ALTERATION

Limonitic and hematitic alteration and veining affect both the mineralized and unmineralized skarn of the inner zone in Mini-Grid. No similar alteration is seen on the south side of the sill. On a small scale, alteration and oxidation of pyrrhotite is invariably present. Pyroxenes and amphiboles show some variable alteration along cleavages. Zones of almost complete limonitic alteration were intersected in most drill holes in the inner

PLATE 13

PLATE 13a. Multiple phase grain of hedleyite, bismuth, joesite (jo) and electrum.
(Bar=0.025mm.)

PLATE 13b. Bismuthinite (bism) replacing bismuth. (Bar=0.025mm)

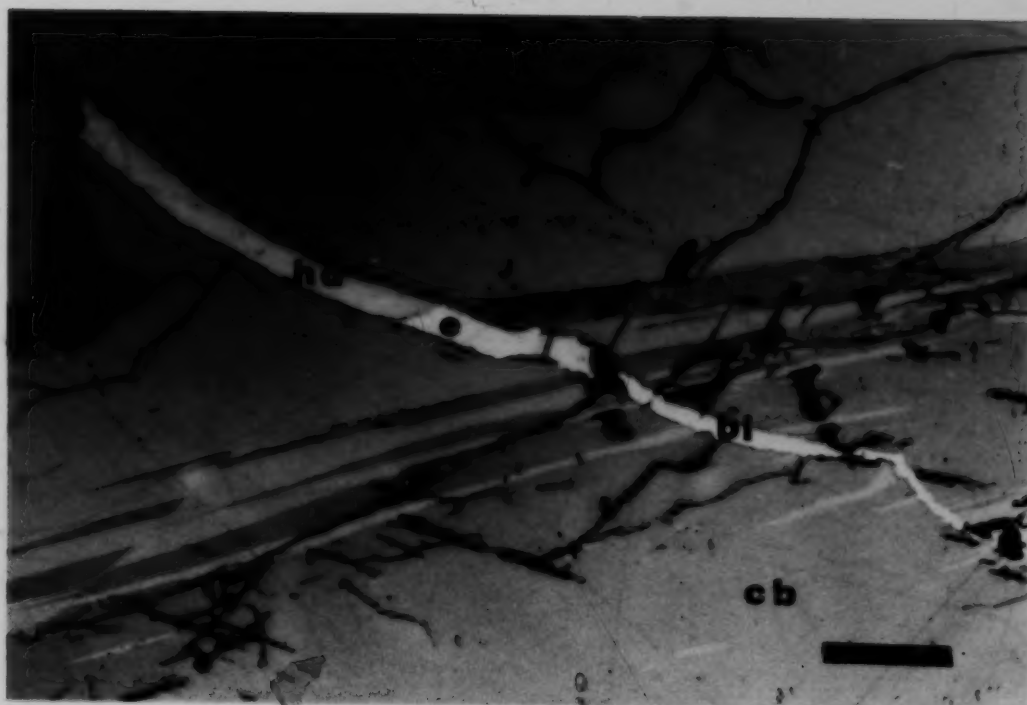
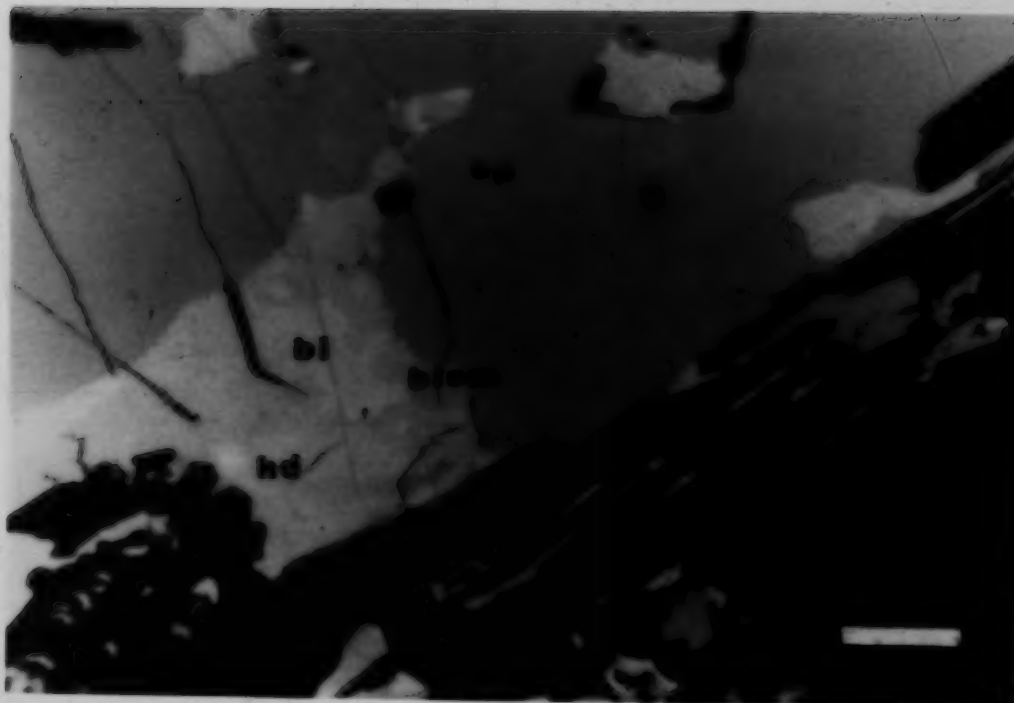


COLOURED PICTURES
Images en couleur

PLATE 14

PLATE 14a. An assemblage of bismuth minerals at the margin of large chalcopyrite grains and in the adjacent gangue. (Bar=0.025mm.)

PLATE 14b. A fracture-filling vein of electrum and bismuth minerals. Mini-Grid.
(Bar=0.05mm.)



COLOURED PICTURES
Images en couleur

PLATE 15

PLATE 15a. Skeletal arsenopyrite in chalcopyrite with later electrum. Mini-Grid.
(Bar=0.05mm.)

PLATE 15b. Exsolution of electrum and bismuth minerals from arsenopyrite. Mineral
Gully (DDH-1). (Bar=0.05mm.)

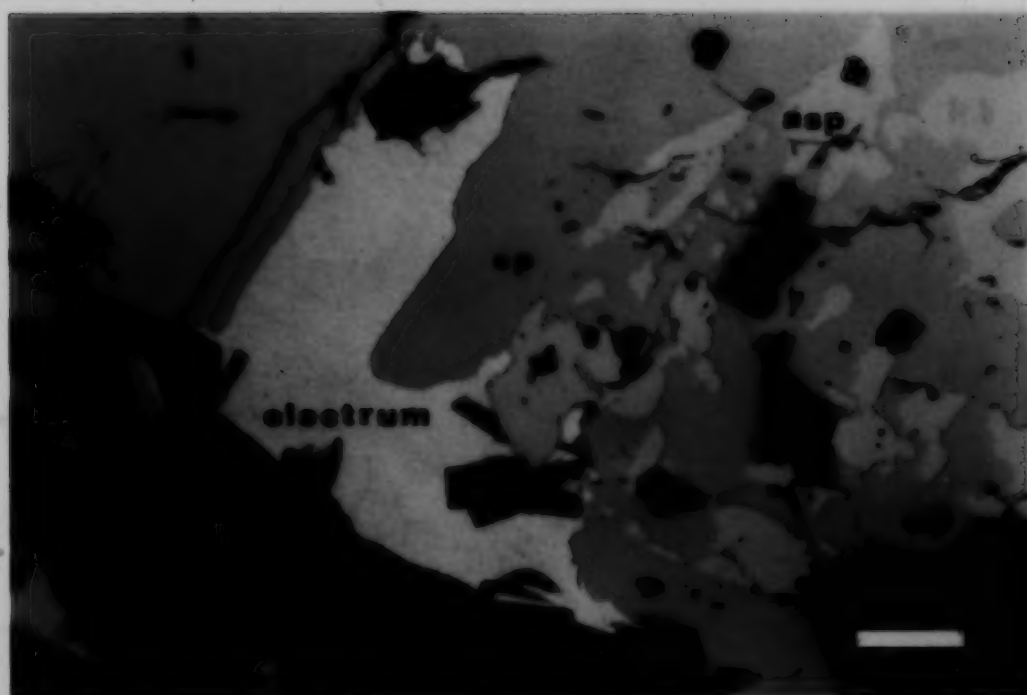


Table 4.1

Analyses of Joselite and Hedleyite

	Joselite 1.	Hedleyite 2.	3.	4.	5.	6.	7.
Bi	77.419	81.864	81.859	82.092	81.815	82.418	81.214
Te	20.410	17.599	17.532	17.742	17.738	17.624	17.678
S	2.600	0.012	0.005	0.000	0.000	0.019	0.017
Fe	0.087	0.114	0.118	0.114	0.179	0.786	0.763
TOTAL%	100.516	99.589	99.514	99.948	99.732	100.847	99.672
	NUMBER OF IONS CALCULATED TO 100						
Bi	60.4266	73.7211	73.7168	73.5737	73.3544	72.0799	71.7886
Te	26.0907	25.8258	25.8572	26.6424	26.0462	25.2429	25.5926
S	13.2284	0.0709	0.0283	0.0000	0.0000	0.1065	0.0957
Fe	0.2543	0.3822	0.3977	0.3839	0.5993	2.5707	2.5231

1. $\text{Bi}_{1.44}\text{Te}_{1.44}\text{S}$
 2. $\text{Bi}_{1.45}\text{Te}$
 4. $\text{Bi}_{1.7}\text{Te}$
 6. $\text{Bi}_{1.6}(\text{Te}_{0.1}\text{Fe}_{0.1})$

STANDARDS:
 BISMUTH METAL
 TELLURIUM METAL
 SPHALERITE
 IRON METAL

Table 4.2

Electrum analyses

	Au%	Ag%	TOTAL%
MINI-GRID	57.196	42.509	99.705
	63.384	36.779	100.163
	58.277	41.953	100.230
	58.331	42.201	100.532
MINERAL GULLY	40.540	60.551	101.091
	48.991	50.850	99.841
	45.166	54.594	99.760

STANDARDS:
ELECTRUM 60.04%Au (gold standard)
ELECTRUM 22.00%Au (silver standard)

zone. (Plate 16a) Calcite, gypsum and secondary copper minerals also belong to this last period of skarn evolution.

The only native gold found on the MARN property occurs in a thin zone of chalcocite, cuprite and iron oxides (Plate 16b). The gold appears to have been preferentially leached relative to silver from the primary electrum during late alteration and oxidation stages.

4.3 SUMMARY AND PARAGENESIS

Similarities in the style and mineralogy of the mineralization on the northern and southern margins of the sill suggest a common mode of origin in the two areas. Processes occurring both before and after the mineralization event produced contrasting skarn and alteration assemblages. Firstly, in Mineral Gully, pyroxenes representing the early stage of skarn formation are relatively iron-rich and constitute a greater percentage of the rock than do the pyroxenes in Mini-Grid. Secondly, the scarcity of actinolite, the lack of late alteration and the absence of secondary copper minerals contrast with the intensely altered inner skarn of Mini-Grid.

In Mini-Grid, an inner mineralized zone, and an outer, barren zone are tentatively distinguished. In the Mineral Gully area, no zone of barren skarn separates the hedenbergitic rocks from the marbles, although a comparable rock type occurs locally. The following comparisons between the inner and outer skarns in Mini-Grid may also be applied to the wollastonite-bearing and iron-rich skarns of Mineral Gully.

1. Quartz is abundant in the inner skarn, forming after the main period of pyroxene skarn development. In the outer skarn, with the exception of the conglomerate horizon, quartz is rare or absent.

2. Pyroxenes of the inner skarn are low in aluminum, and more iron-rich than their counterparts in the outer skarn (Figs. 4.8a, 4.8b).

3. Aluminous phases are rare in the inner skarn and confined to skarn in the more aluminous hornfels protolith. Anorthite, grossular garnet and aluminous pyroxenes are common in the outer skarn.

4. In the outer zone, skarn only formed in the limestone horizon, whereas in the inner zone, almost identical skarn is developed in both the limestone and the underlying

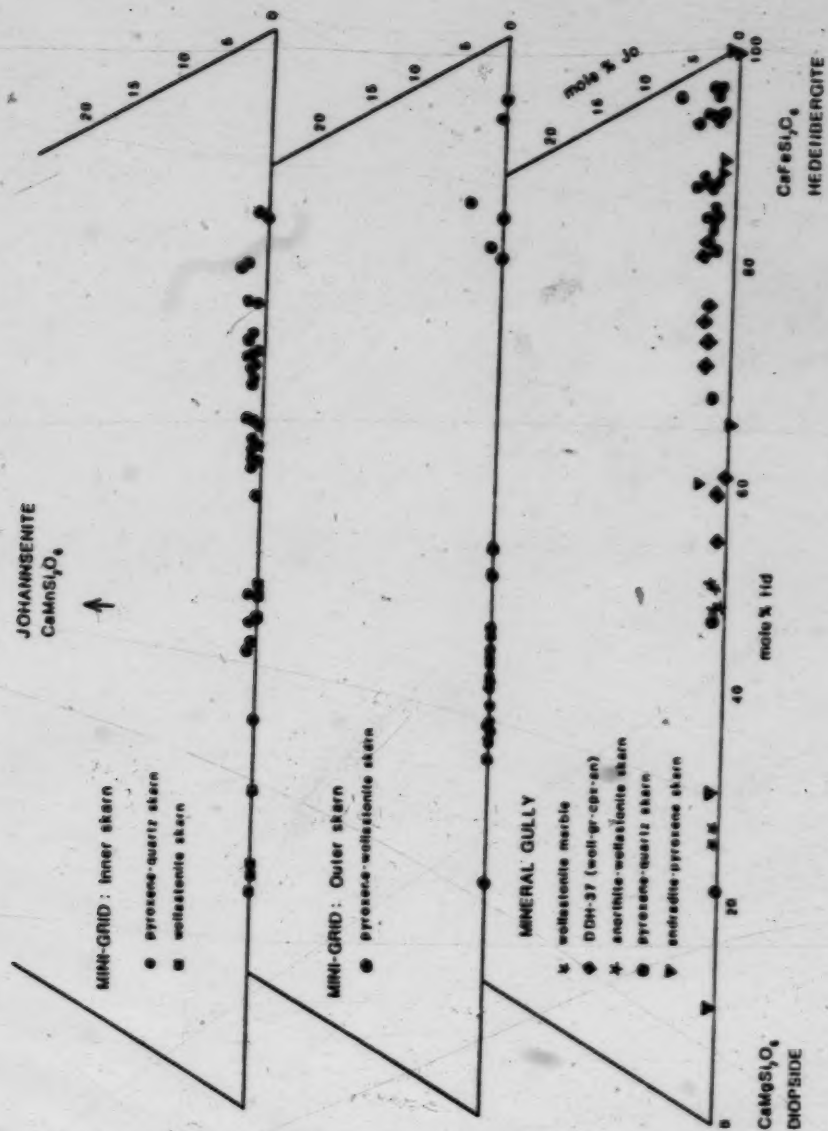


Figure 4.8. Composition of pyroxenes from the Mineral Gully and Mini-Grid areas in terms of the Fe-Mg-Mn end-members.

PLATE 16

PLATE 16a. High-purity gold (au) in a matrix of chalcocite, and iron oxides. Mini-Grid,
(Bar=0.05mm.)

PLATE 16b. Samples of the intense limonitic alteration in monzonite sills (A) and
pyroxene skarn (B) from Mini-Grid.



COLOURED PICTURES
Images en couleur

hornfels.

5. Wollastonite is absent in the inner skarn with the exception of one location marginal to the main altered horizon; however, it is a major phase in the outer skarn where it was the earliest formed mineral.

6. Abundant actinolite replacing pyroxenes in the inner region represents the first stage of hydrous retrogressive alteration of the primary skarn. No equivalent is present in the outer skarn.

7. Pyrrhotite and chalcopyrite heavily replace skarn silicates in the inner zone, while they are absent or very minor in the outer skarn.

8. Limonite and secondary copper minerals form a late destructive stage in the inner zone that is absent in the outer skarn.

In the detailed parageneses of the different skarn types recognised in the MARN, which are illustrated in Figures 4.4-4.7, the length of the horizontal bar represents an estimate of the relative time period over which that mineral formed based on the importance of each mineral present.

All five stages in the evolution of the skarn are identified in the mineralized zones of Mini-Grid and Mineral Gully. No attempt is made to correlate events in the iron-rich skarns with those in the wollastonite-bearing skarns, with the exception of the contact metamorphic stage.

4.4 LITHOLOGICAL CONTROLS ON SKARN FORMATION

Lithological controls on the distribution of skarn and mineralization are important, both in Mineral Gully and Mini-Grid; however, their effects are more complex on the northern side of the sill. The isolated skarn lenses seen in the creek bed of Mineral Gully (Plate 2) are confined by the regular, quartz-rich horizons in the Tahkandit Limestone. In the massive skarn, however, even the quartz-rich layers are replaced. Hedenbergitic skarn in this area is located in the upper part of the Tahkandit Limestone, with the low-grade mineralization confined to the top of this unit. A similar relationship is seen in some drill core sections from Mini-Grid, but the overall pattern is generally more complex.

In the northern skarn body, the location of the skarn horizon is unpredictable. Lithological contacts may be the site of mineralization in one hole, but barren in the next. The pattern is complicated by the numerous monzonite sills. Rather than a single, common heat source that the upper sill provided on the south side, these small sills may each have acted as a local heat source.

On the northern side of the sill, the Tahkandit Limestone is almost a third of the thickness that it is to the south. Fluid circulation was probably concentrated to a greater extent in the thinner carbonate unit of Mini-Grid. This may have contributed to the degree of alteration seen in the friable calcareous horizon beneath the skarn lenses that is seen in Mini-Grid (Chap. 4).

A major factor controlling fluid circulation during the later skarn stages was the porosity and permeability of the rocks subsequent to the early period of pyroxene skarn formation. It is probable that the very low volume of vug spaces remaining after the hedenbergite skarn formed was important in limiting the degree of fluid circulation, and thereby restricting the amount of later alteration. In Mini-Grid, the greater amount of open spaces after the early stage, gave the skarn a greater permeability, and allowed later fluids to interact with a greater volume of pyroxene skarn. Textures in the Mini-Grid skarn seem to confirm this where occasional massive pyroxene skarn, with no calcite or quartz space filling, is unaffected by all later alteration stages, while showing a high degree of replacement by pyrrhotite.

4.5 GOLD MINERALIZATION AND METAL GRADES

Two associations of the gold-bearing assemblage are noted; the occurrence of electrum with arsenopyrite, and the proximity of blebs and veinlets of bismuth, hedleyite electrum and bismuthinite to chalcopyrite, in particular to cubanite exsolution in chalcopyrite.

Textural evidence from DDH-1 suggests that bismuth and electrum formed by exsolution from arsenopyrite; however, no clear exsolution relationship is seen elsewhere. The association of electrum and arsenopyrite noted in several samples from Mini-Grid may be the result of the exsolution of gold and silver from the arsenopyrite on cooling or the coagulation of small inclusions of these metals. This might account for the

association of electrum and arsenopyrite; however, the veinlets of gold and bismuth minerals suggest that deposition occurred predominantly from an aqueous fluid. A period of slight fracturing and the inversion of a high-temperature, copper-iron sulphide phase to cubanite and chalcopyrite occurred between the main phase of sulphide deposition and the electrum-bismuth mineralization. The gold-bearing assemblage is located close to the margin of chalcopyrite veins and aggregates, but rarely within pyrrhotite. Gold and silver were probably present in the mineralizing fluids during the deposition of the sulphides, being incorporated within the lattice structure of arsenopyrite. However, precipitation of the bismuth and gold phases did not occur until some time after the deposition of chalcopyrite.

Native gold was found in a zone of chalcocite, cuprite and other secondary copper minerals within altered monzonite. Development of secondary copper mineralization in this and other zones, may be analogous to the supergene sulphide zones of auriferous sulphide deposits which often contain native gold (Boyle, 1979).

Although gold was not observed in limonitic alteration zones, assay values of up to 200ppm (0.80oz / T), suggest that some degree of concentration occurred. The limonitic zones of Mini-Grid represent the areas of greatest alteration and probably the sites of the greatest fluid flow during the late stages. They are possibly analogous to the supergene oxidized zones of many sulphide deposits. The gold values from the Mini-Grid are too variable to determine if there is any significant concentration of gold in these limonitic zones over unaltered skarn.

METAL GRADES AND DISTRIBUTION

Most skarn intersections from the drill core were assayed for gold, silver, copper and tungsten. The close correlation found between gold, silver and copper is to be expected from the assemblages. The continuity of high grade mineralization in the Mini-Grid is very poor, a feature typical of many skarns, and matches the heterogeneity of the skarn itself. Mineralization occurs exclusively in iron-rich pyroxene skarn and the immediately adjacent hornfels and monzonites. Within these rock types, no metal zoning has been recognised. Sphalerite is the main sulphide phase in an occurrence of actinolite and pyrite-bearing calcareous skarn below the ridge outcrop of the Tahkandit Limestone in Mini-Grid. There is insufficient data to more than tentatively suggest that a weak, outer,

zinc-rich mineralization existed. Locally significant tungsten grades, reaching 5.3 wt% WO_4 , correspond to high copper values; however, there is no consistent relationship between tungsten and the other metals assayed. Remobilization of early scheelite into veins with chalcopyrite may account for the exceptions.

In Mineral Gully, the hedenbergite skarn shows very low metal values. A maximum of 1.3ppm (0.05Oz/T) of gold was recorded over a short thickness of massive pyrrhotite and chalcopyrite mineralization. The highest copper values of 1.5wt% are found in the same zone. In the bulk of the Mineral Gully skarn, the gold, silver and copper values were below 52ppb, 1300ppb, and 0.01wt% respectively.

5. CONDITIONS OF SKARN FORMATION AND MINERALIZATION

5.1 INTRODUCTION

In the preceeding chapters the mineral assemblages of several types of skarn from the MARN have been described in some detail. It is the aim of this final section to integrate the paragenetic relationships and phase equilibria in order to constrain the P-T conditions during skarn formation, and, where possible, to place limits on the composition of the mineralizing and skarn forming fluids. The characteristics of the early skarn period had implications for the later mineralization and are important to the potential economic value of the MARN. The significance of lithological, chemical and geological features in controlling the location of the skarn, are re-emphasized.

Figure 5.1 summarizes the skarn stages in the three main skarn types; the hedenbergite skarn of Mineral Gully, the iron-rich skarn of Mini Grid, and the wollastonite-anorthite skarns found in both areas.

5.2 THE EARLY SKARN STAGE

The early skarn assemblages are dominated by intermediate to iron-rich pyroxenes of the diopside-hedenbergite series. At least four types of skarn are distinguished on the basis of the iron content of the pyroxenes (Fig.5.2), each of which were discussed in some detail in Chapter 4.

In the northern and southern areas both barren and aluminous skarn are present. The mineral assemblages include valuable indicators of the temperatures attained during the early skarn period. Most important is the coexistence of anorthite and wollastonite which gives a minimum temperature of approximately 600°C. This and other reactions involving aluminous phases in a CO_2 - H_2O mixture, are conveniently plotted on a T-X CO_2 diagram (Fig.5.3).

5.2.1 IRON CONTENT OF THE SKARNS

Figure 5.2 emphasises the contrast between the chemistry of the skarn types in the MARN. The pyroxene compositions of the inner skarn of Mini-Grid show a much greater range than do those of the hedenbergitic skarn of Mineral Gully. The pyroxene

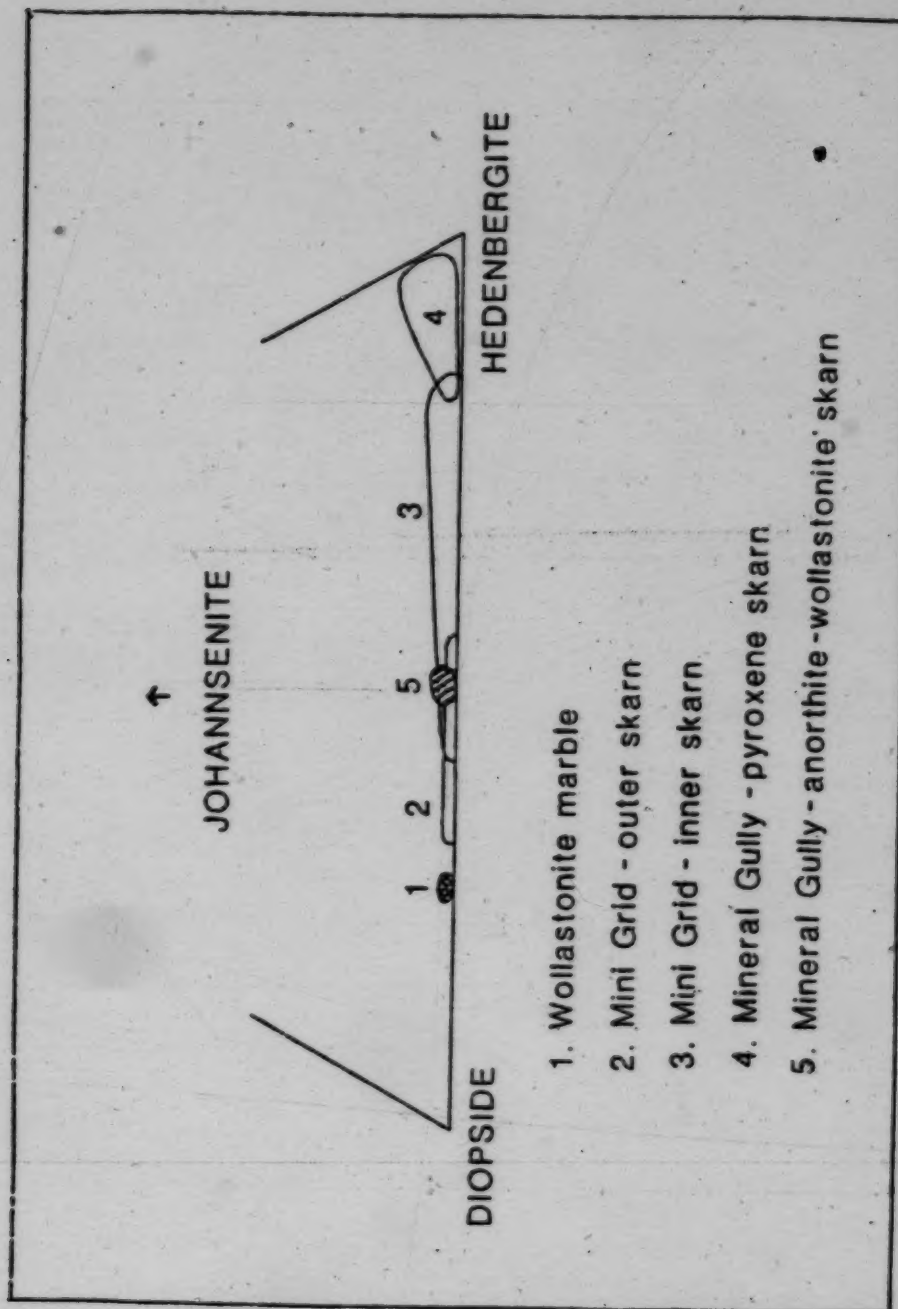


Figure 5.2. Compositional variations between pyroxenes of the different skarn types simplified from Figure 4.8.

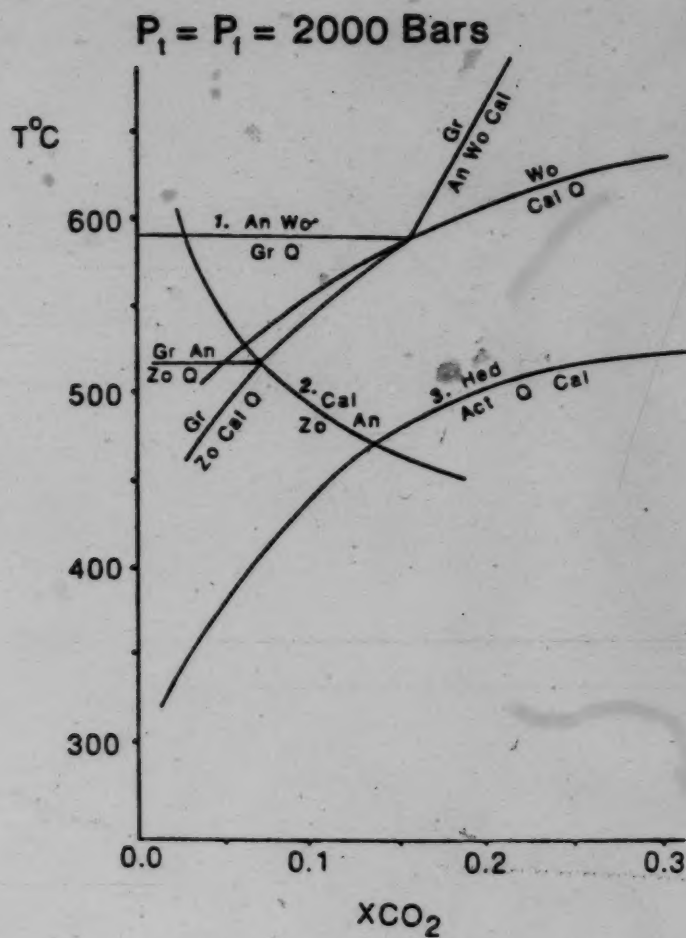


Figure 5.3. T-XCO₂ diagram of equilibria in the system Ca-Al-Si-C-O relevant to the barren, wollastonite-bearing skarns of the MARN, after Gordon and Greenwood (1971). Reaction 3. from Shoji (1980).

compositions from the iron-rich skarn of Mini-Grid overlap both those of the outer skarn in Mini Grid, and the similar wollastonite-bearing skarn of Mineral Gully; however all have distinctly higher iron contents than the metamorphic pyroxenes of the marbles.

The relationship between the wollastonite-bearing and iron-rich skarns is ambiguous. Generally in most well zoned skarns, the zones are developed in a consistent pattern at all marble contacts (Einaudi et al., 1981). At the MARN, the skarn-marble contact is only well exposed in Mineral Gully, where there is no zoning parallel to either the marble or the intrusive contacts. It is therefore unlikely that the wollastonite-bearing skarns represent part of a classic skarn zoning sequence. The overall chemistry of this skarn type is more aluminous than the hedenbergitic rocks. The absence of quartz and the presence of pyroxenes containing a significant Tschermak component suggests that the skarn-forming fluids were slightly undersaturated in silica. At least two mechanisms might account for the formation of these low-iron and high alumina skarns. Firstly, they might have developed almost simultaneously with the iron-rich skarn, but represent the first interaction of fluids with carbonate rocks. At high temperatures magnesium is strongly partitioned into the silicate phases, while iron remains in the fluid phase. Fluids coming into contact with the reactive carbonate rocks for the first time, at temperatures in excess of 600°C, would become depleted in magnesium after the formation of diopsidic pyroxenes. The remaining fluids enriched in iron, and possibly at a slightly lower temperature, subsequently form more iron-rich pyroxene skarn.

Alternatively, the low-iron skarn might represent a slightly earlier fluid pulse of magmatic origin. The higher temperatures caused a greater degree of magnesium fractionation into the pyroxenes, and might explain the greater mobility of aluminum in these fluids.

The local development of these more aluminous skarns suggests that they represent only a minor event in the overall skarn development, or that they were more extensive and were overprinted by later Fe-rich skarn. The only evidence for the latter is seen in the sample of andradite-bearing float described in Chapter 4. The diopside cores may be the result of a period of early magnesium metasomatism similar to that described by Meinert (1984) in magnetite skarns.

The difference in the iron content of pyroxenes from the northern and southern skarns may also be the result of variations in the Fe/Mg fractionation between fluid and silicates possibly resulting from different temperatures in the two areas.

5.2.2 FLUID COMPOSITION

Skarn fluids are essentially water-rich CO_2 - H_2O mixtures. The fluid composition is not easily constrained. Zoisite is only stable in water-rich fluids, and its absence in the MARN rocks gives a minimum XCO_2 value to the skarn fluids from reaction 2, in Figure 5.3.

Two of the most important controls on mineral stabilities are the fluid composition (XCO_2) and the oxygen fugacity. The stabilities of common skarn assemblages in the Fe-Ca-Si-C-O system are shown in $\log f\text{O}_2$ - $\log f\text{CO}_2$ plots calculated at 500°C and 600°C, in Figures 5.4 and 5.5. All the reactions were calculated using the FORTRANIV program SUPCRT (Helgeson, 1978). All the reaction constants are included in Appendix 2. The magnetite-quartz-fayalite oxygen buffer (QFM) from Kerrick and Ohmoto (1977), which is included for comparison, is at a lower $f\text{O}_2$ than that calculated by SUPCRT. Decreasing the activity of iron in hedenbergite and andradite effectively moves the invariant point A to higher $f\text{O}_2$ and $f\text{CO}_2$, increasing the stability fields of the pyroxene-bearing assemblages. For simplification in calculating the effect of increased diopside components on the equilibria, the assumption was made that the activity of iron in pyroxenes and garnet were the same, which is not accurate; therefore the positions of the equilibria are only qualitative.

The shaded areas represent the probable $f\text{O}_2$ - $f\text{CO}_2$ range in the early skarn. Magnetite occurs only rarely in the southern area. Hedenbergite and wollastonite appear to be an incompatible assemblage in massive skarn; however, they do occur together in pyroxene veins and lenses beyond the main skarn front. In these areas, reaction 3 provides a maximum limit to $f\text{O}_2$, while in the massive skarn, $f\text{O}_2$ is limited by reaction 2. The only occurrence of andradite is in the sample of float mentioned previously. The replacement of andradite by calcite, hedenbergite and pyrrhotite probably represents a reaction in the Ca-Fe-Si-C-O-S system such as:

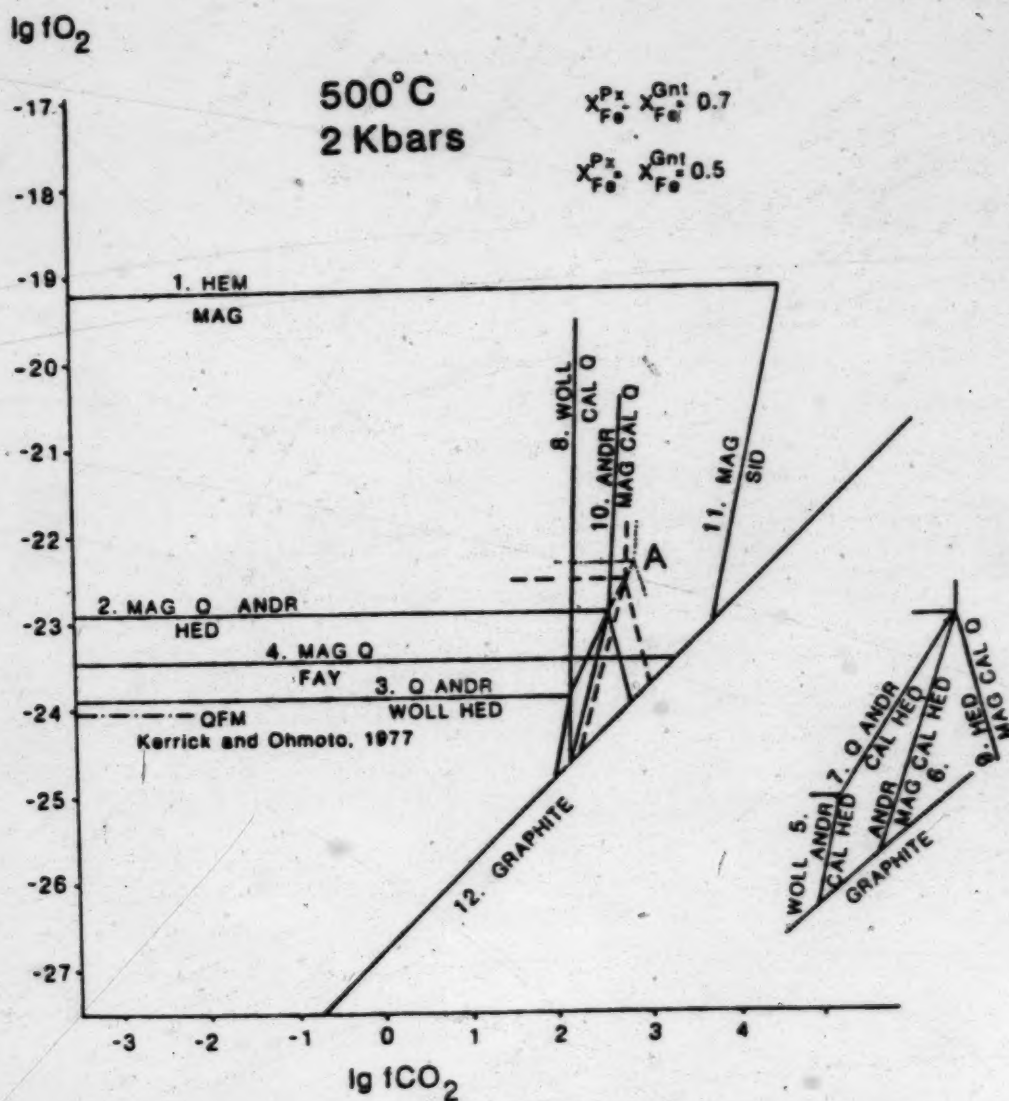


Figure 5.4. LogfO₂-LogfCO₂ diagram at 500°C and 2Kbars, calculated for common skarn assemblages in the system Ca-Fe-Si-C-O, using SUPCRT. The shaded region represents the fO₂-fCO₂ range of the MARN skarn silicates. The effect of decreasing the activity in pyroxenes and garnets is shown qualitatively by the broken and dotted lines.

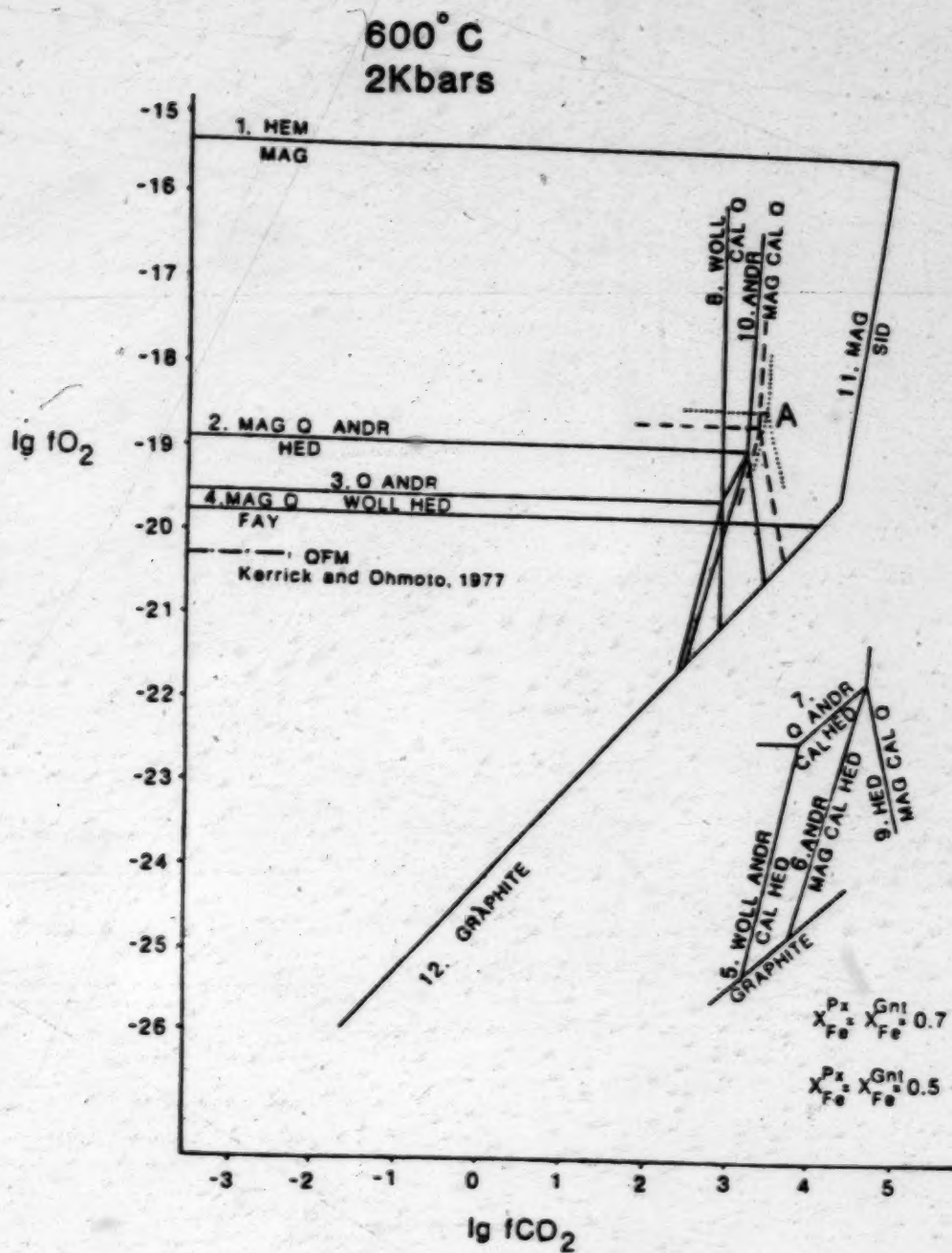
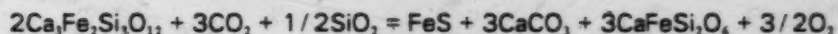


Figure 5.5. LogfO₂-LogfCO₂ diagram at 600°C and 2Kbars for the system Ca-Fe-Si-C-O, calculated using SUPCRT.



which cannot be represented in figures 5.4 and 5.5. Graphite is absent in all skarnified rocks, so that the graphite stability curve represents a minimum $f\text{O}_2$. A comparison of the actual mineral assemblages with figures 5.4 and 5.5, suggest that $f\text{CO}_2$ and $f\text{O}_2$ were externally controlled. Local buffering, for example by the mineral reactions, would result in invariant assemblages, which are not seen. There is no problem in evolving the reduced fluid necessary to produce the prograde skarn assemblages of the MARN. Fluids passing through either of the hornfels units would be reduced by reaction with graphite, while the intrusive contains ilmenite and probably evolved relatively reducing fluids.

5.2.3 RETROGRADE ALTERATION

A hydrous, retrograde alteration assemblage of calcite, actinolite and quartz replaces iron-rich pyroxene skarn, and precedes the mineralization stage. The reaction involved is plotted on the T- $f\text{CO}_2$ diagram in Figure 5.3 using the results of Shoji (1980). Zoisite is absent in this stage, and therefore, the temperature range over which the retrograde alteration occurred may be restricted by curve 1 to 470°C to 550°C. Pyrrhotite appears to follow the formation of actinolite closely, so that this may also be considered as the maximum temperature for the first sulphide deposition.

5.2.4 THE SIGNIFICANCE OF EARLY SKARN FOR LATER MINERALIZATION

The pyroxene skarn exerted both chemical and physical controls on later mineralization. The sulphides, in particular pyrrhotite, replace hedenbergitic skarn, and there is little doubt that at least some of the iron was derived from the silicates during the replacement process. This is supported by the fact that most of the mineralization is restricted to iron-rich skarn. The permeability of the skarn itself controlled the degree of the fluid-skarn interactions, and therefore the extent of mineralization. The permeability of the Mineral Gully and Mini-Grid skarns are discussed in some detail in Chapter 4.

5.3 MINERALIZATION

5.3.1 ENVIRONMENT OF DEPOSITION

Two stages of mineralization are distinguished; the deposition of sulphides followed by gold and bismuth mineralization. The sulphides show a close spatial relationship with actinolite, but consistently replace both the skarn pyroxene and amphibole. The association of mineralization with the slightly earlier retrograde assemblage suggests that sulphide deposition began quite soon after the period of retrograde alteration, and consequently the maximum temperature for mineralization was about 480°C. There are no other thermometers that are directly applicable to sulphide deposition.

Deposition of bismuth and gold minerals occurred after a period of fracturing and brecciation. The presence of hedleyite in the assemblage indicates a maximum temperature of 312°C (1 bar) for deposition (Figure 5.6). Bismuth has a melting point of only 271°C; however, it is difficult to determine whether it was ever in the liquid state. At 1-2 Kbars, contraction cracks in sulphides caused by the cooling of bismuth, would probably have been resealed.

Figures 5.7a and 5.7b give an indication of fO_2 - fCO_2 conditions during mineralization. Pyrite is absent from the primary mineralization and occurs only as a fine grained alteration of pyrrhotite and replacing cubanite. The coexistence of pyrrhotite and arsenopyrite restricts $\log fS_2$ to a range of -11 to -8 for the main period of mineralization at. The replacement of pyrrhotite by pyrite, and bismuth by bismuthinite may indicate an increasing fS_2 or simply the effect of falling temperature on the relative stabilities of these minerals. fO_2 is not well constrained; however, the presence of magnetite early in the paragenesis of the southern skarn suggests that fO_2 was slightly higher in this area.

The fO_2 - fS_2 range shown in figures 5.7 is in agreement with that established by Sato (1980) at the Fujigatani tungsten mine in Japan, which also shows some bismuth mineralization.

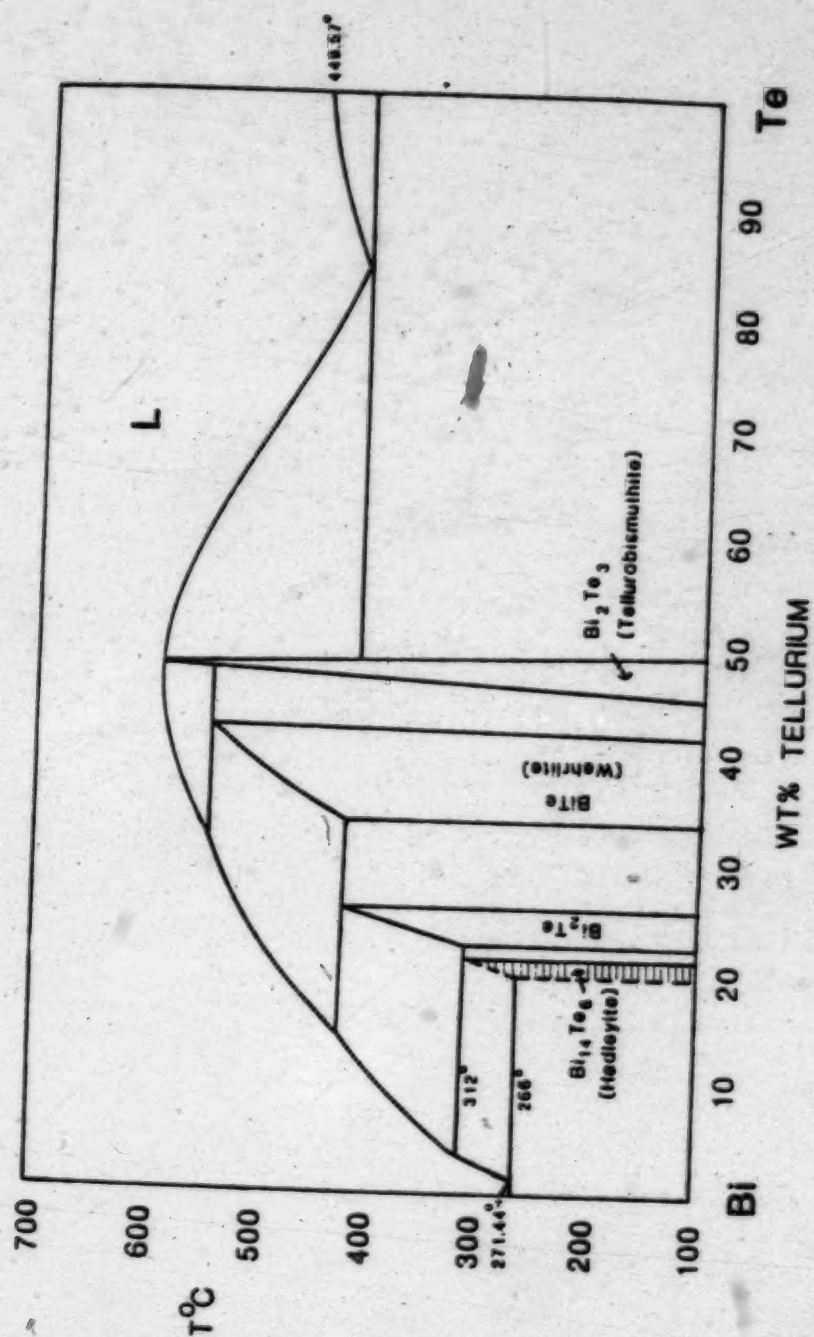


Figure 5.6. The Bismuth-Tellurium system, after Hawkins and Holtgren, 1973.

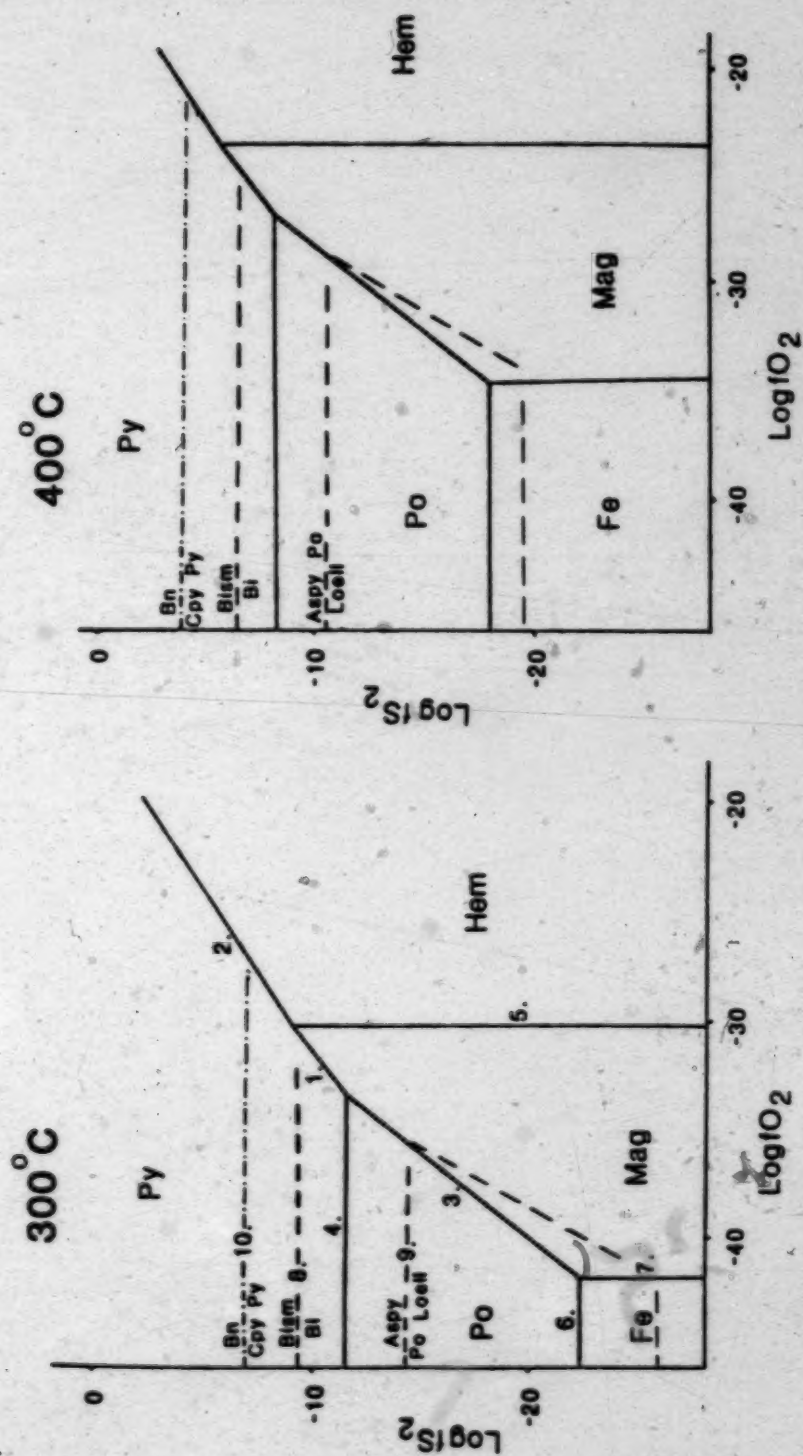
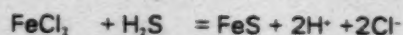


Figure 5.7. LogfS₂-LogfO₂ diagrams of the iron oxide and sulphide minerals over the temperature range of sulphide mineralization at the MARN. Data for Fe sulphides and oxides and for bismuth and bismuthinite from Robie et al. 1978. Chalcopyrite-bornite and loellingite-arsenopyrite stabilities from data in Barton and Skinner, 1977.

5.3.2 METAL TRANSPORT AND DEPOSITION

Temperature and oxidation state of the fluids are considered to be the most important influences on the mobility of metals in the few skarns where this has been discussed. Most of the gold-bearing skarns of Japan contain oxidized mineral assemblages and it is concluded that oxidizing fluids transport more gold than reduced fluids (Shimazaki, 1980). In contrast, mineralogical and geological evidence from the MARN indicates that skarn-forming fluids were relatively reduced.

Pyrrhotite-chalcopyrite-(arsenopyrite) mineralization at the MARN occurred at temperatures in excess of 300°C. At these temperatures ferrous iron is increasingly associated with Cl^- , while at lower temperatures, chloride complexes are ineffective in transporting large amounts of iron (Barnes, 1979). Similarly, copper is transported as chloride complexes at the temperatures of the sulphide mineralization. The most likely cause for sulphide deposition is by falling temperature. The deposition mechanism:

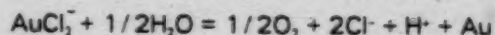


also produces hydrogen ions which must be available in order for the replacement of skarn silicates by sulphides to occur.

Deposition of the gold-bismuth-tellurium assemblage occurred below 300°C. At these temperatures replacement is not an important process (Rose and Burt, 1979), and consequently veining is the main style of mineralization. Again, deposition probably occurred as a result of the falling temperatures. There are little published data on bismuth or tellurium mobility and complexing. Telluride complexing of gold may be important where the total amount of sulphur is low. The two most discussed complexing ligands of gold are the chloride and sulphide species. Sulphide complexes of gold are the most dominant particularly at lower temperatures and under more reducing conditions (Seward, 1973). Gold was in solution during the earliest sulphide deposition indicated by the exsolution of bismuth and electrum from arsenopyrite. The temperature of arsenopyrite deposition was probably in excess of 400°C; therefore it appears that gold was in solution at high temperatures.

The relative importance of the sulphide and chloride ligands is a function not only of T , $f\text{O}_2$ and pH , but also of the total concentration of the available ligands. Very saline fluid inclusions of up to 35wt% NaCl equivalent were observed in a few samples of quartz

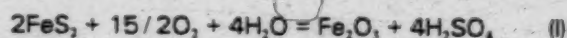
and suggest that the total chloride concentration was high. It is proposed that gold was in solution mainly as chloride complexes at high temperatures, being deposited when the complexes became unstable at some temperature below 300°C by mechanisms such as:



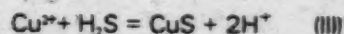
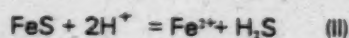
A similar process for the transport of bismuth and silver may be suggested.

5.4 LATE OXIDATION AND ALTERATION

It was suggested in chapter 4. that one of the causes of heterogeneous mineralization and higher local gold values in the northern skarn was the secondary oxidation and enrichment of primary sulphide and gold-bearing minerals. The enrichment of gold and silver in surface oxidation and supergene sulphide zones of auriferous sulphide deposits is widely reported (Boyle, 1979; Krauskopf, 1979). The oxidation of sulphides above the ground-water table produces an acidic solution;



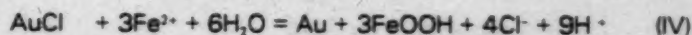
Copper, in particular, is more soluble in oxidizing conditions and is carried in solution until it comes into contact with primary sulphides. At the contact of oxidized and unoxidized sulphides, which usually coincides with a present or former water-table, copper is reduced by the unaltered sulphides and may displace other metals, particularly iron and zinc (Krauskopf, 1979). Acidic solutions formed during oxidation may dissolve primary sulphides to form H_2S or HS^- , which may then promote the precipitation of copper sulphides.



These two processes result in an enriched zone of chalcocite, covellite and other copper sulphides between the zone of oxidation and the primary sulphide ore. Silver shows similar behaviour where argentite (Ag_2S) and pyrargyrite (Ag_3SbS_3) are common secondary minerals in the supergene sulphide zone. Silver chloride may be found in the oxidized zone.

Supergene enrichment of gold has been described. Mann (1984) discusses mechanisms of silver and gold mobility in the oxidized environment of lateritic weathering profiles. In acidic and chloride-rich solutions, gold and silver form chloride complexes.

Reduction by ferrous iron preferentially precipitates gold while silver remains in solution. The association of high-purity gold with limonite may be the result of the simultaneous precipitation of the two by reactions such as:



In the northern skarn body of the MARN limonite is widely developed and often replaces skarn completely. Secondary copper mineralization is more limited, occurring in narrow zones within altered monzonite. Their appearance suggests that they were originally sulphide veins, while the textures suggest that secondary minerals replace primary cubanite and chalcopyrite. Covellite replaces cubanite in a number of samples in the primary mineralized skarn (Plate 12) suggesting that these processes are quite widespread. It is not possible to determine whether the high-fineness gold resulted from insitu leaching of silver or was deposited from solution.

Iron oxide replacement varies from incipient alteration of pyroxenes and sulphides, to complete replacement of massive skarn. Several mechanisms might have been important, including the hydrolysis of ferrous iron to form limonite and the oxidation of sulphides (Reaction I). The acidic solutions produced by these processes would attack skarn silicates, releasing more ferrous iron.

The limonitic and chalcocite zones, although rarely closely related, may be linked by similar processes to those described above for supergene sulphide and oxide zones.

The supergene alteration zones of sulphide deposits are usually the result of interaction with ground water close to the water table. The most deeply altered deposits, such as the Rosita mine in Nicaragua (Bevan, 1973), were at low latitudes and in regions of heavy rainfall at some time in their history. The MARN is not comparable in several respects. Firstly, the northern skarn, which shows the greatest degree of alteration, is completely concealed by the upper monzonite sill. The southern skarn, which is exposed, shows no supergene alteration. Secondly, the Tombstone area has been at latitudes greater than 60°N since the emplacement of the Mount Brenner Stock, and it is unlikely that groundwater was responsible for the alteration. It is probable that this represents a final oxidation stage related to the main skarn event.

5.5 COMPARISON OF THE MARN WITH OTHER SKARN TYPES

Of the major skarn types described in Table 2, the MARN bears the greatest resemblance to reduced tungsten skarns, such as those of Japan and Canada. All of these are characterized by hedenbergite-rich, prograde skarn assemblages. Reduced skarns, such as the pyrrhotite-rich scheelite deposit of MacTung in the Yukon (Dick and Hodgson, 1982) and the Fujigatani mine in Japan (Sato, 1980) are a group of skarns that formed at a relatively deep level and are characterized by a lack of endoskarn development. More diverse metal associations, such as the Cu-W-Zn-Sn-Ag-Au assemblage of the Kuga mine (Shimazaki 1980), are relatively uncommon. The MARN is a polymetallic body, enriched in copper, gold, silver and tungsten, with very minor zinc. It clearly does not fit into the same class as the tungsten skarns, although the environment of formation appears very similar. Gold is a common but minor component of hedenbergite-rich skarns. The MARN is therefore unusual in that gold is significantly enriched.

Most skarns that are important primarily for their gold, have more oxidized assemblages, such as the cobalt-bearing magnetite skarns described by Meinert (1984). Einaudi (1980) identified a distinct group of copper skarns associated with barren stocks. Typically these have a polymetallic association more akin to that of the MARN. Another similarity is the common gangue assemblage of hedenbergitic pyroxene and grossular garnet. This group includes some important gold deposits notably the Rosita mine in Nicaragua. The MARN can therefore be categorized as a 'reduced, polymetallic gold-bearing skarn.

5.6 SUMMARY AND CONCLUSIONS

The skarns of Mineral Gully and Mini Grid are characterized by several distinct stages. Some of the most important features of each are summarized below.

1. Contact metamorphism reached temperatures in excess of 600°C at 2Kbars. The siliceous Tahkandit Limestone formed wollastonite-diopside marbles in the thermal aureole.
2. The main stage of metasomatism resulted in the formation of massive and almost monomineralic, iron-rich pyroxene skarn. The assemblage is notable for the absence of garnet. The fluids originated from an unknown source, however it is probable

that they included a significant magmatic component during the early stages. Endoskarn development in the intrusive was restricted to minor pyroxene-feldspar veins, while the only evidence of any interaction of skarn fluids with the monzonite is often the absence of biotite and an abundance of sphene in the otherwise unaltered intrusive.

Movement of skarn-forming fluids was essentially controlled by impermeable lithological units. In the southern skarn the upper hornfels acted as a cap rock, resulting in massive, homogeneous skarn development in the upper part of the Tahkandit Limestone. Figure 5.8 illustrates the more complex situation in the Mini Grid area. The alteration of the relatively unreactive lower hornfels probably resulted from the entrapment of fluids beneath small monzonite sills. A significant result of the prograde stage was the formation of a secondary porosity, controlled by the amount of open space remaining after pyroxene growth. The southern skarn shows significantly less open space filling, possibly as a result of extended pyroxene growth due to slower cooling rates.

3. Retrograde alteration of pyroxene skarn to an assemblage of actinolite, calcite and quartz, occurred at approximately 500°C. The degree of alteration appears to be related to the porosity of the skarn and only slightly affects the southern area.

4. Sulphide mineralization occurred between 480°C and 300°C. Sulphur fugacities can be restricted by the assemblage of pyrrhotite and arsenopyrite, and by the absence of pyrite, to $\log fS_2 = -10(400^\circ\text{C})$. fO_2 in the southern skarn may have been slightly higher than in the north, suggested by the presence of magnetite with pyrrhotite. The restriction of sulphides to iron-rich skarn indicates some degree of dependancy on the chemistry of the gangue silicates which were probably the source of at least some of the iron, now forming the sulphides.

5. Gold and bismuth minerals were deposited from chloride complexes at temperatures below 300°C. Gold, bismuth, silver and tellurium were present in solution during earlier sulphide mineralization, and the deposition of these minerals with falling temperatures was an extension of the same mineralization process.

6. A period of late alteration of skarn to iron oxides and hydroxides was intensely developed only in Mini Grid and again, permeability was a controlling factor. Secondary copper minerals, developed by the insitu replacement of primary chalcopyrite and cubanite, are associated with high-purity gold.

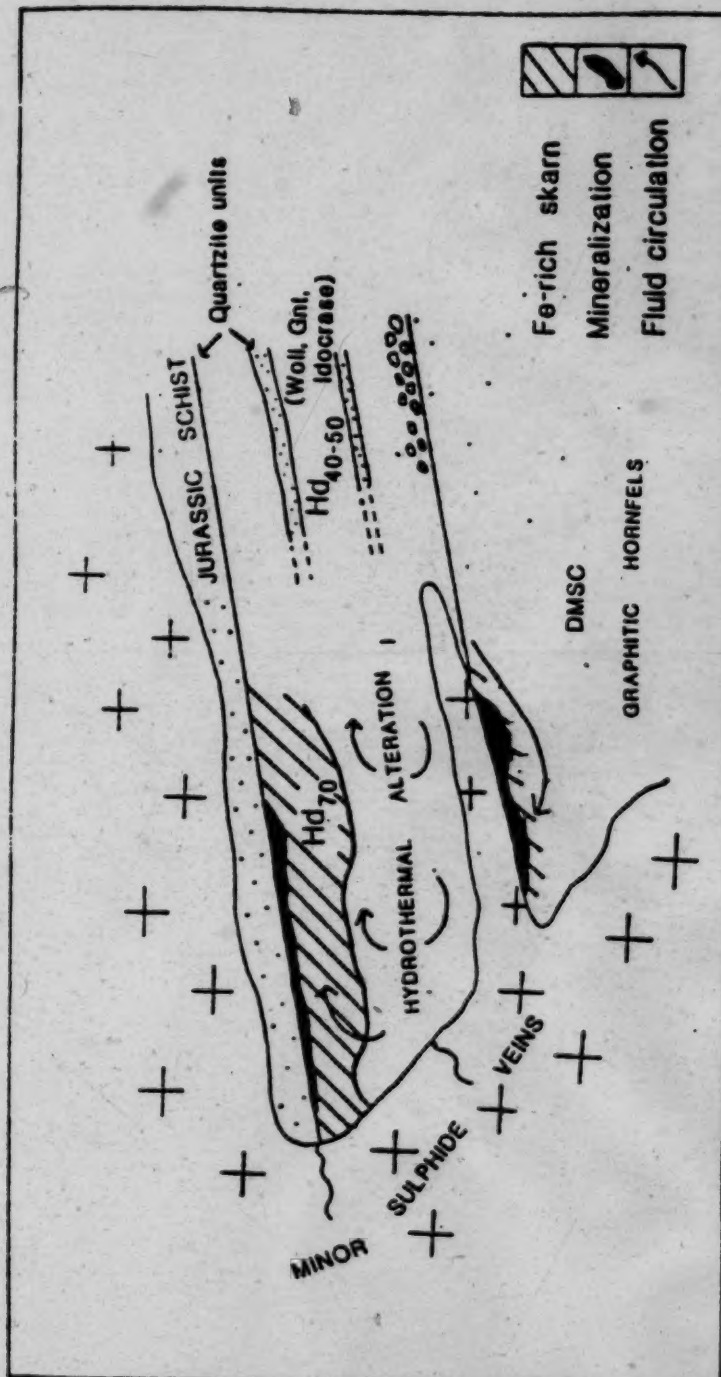


Figure 5.8. Idealized section through the Mini-Grid skarn showing some of the features of the Inner and Outer skarns.

These stages of skarn development are reflected in the pattern of mineralization. The volume of the sulphide and gold-bearing assemblages is directly related to the permeability of the skarn after pyroxene growth. The higher permeability of the northern skarn allowed a greater degree of fluid/ skarn interaction, resulting in intense retrograde alteration and mineralization. The intensity of fluid concentration between the upper and lower sills in Mini Grid has no parallel in Mineral Gully. It appears then that the low grades of gold, silver and copper in Mineral Gully result from the processes described above. In the light of this, it is unlikely that significant gold values would be found in the skarn on the southern margin of the main sill.

REFERENCES

- Barnes, H.L., 1979, Solubilities of ore minerals: *in* Barnes, H.L., 1979, Geochemistry of hydrothermal ore deposits: New York, Wiley, p. 404-460.
- Barton, P.B., and Skinner, B.J., 1979, Sulfide mineral stabilities: *in* Barnes, H.L., Geochemistry of hydrothermal ore deposits: New York, Wiley, p. 278-403
- Bevan, P.A., 1973, Rosita Mine - A brief history and geological description: Can. Inst. Min. Metall., Bull. v. 66, no. 736, p. 80-84.
- Biczok, J., 1981, Geology and drilling, MARN 1-108 claims, Mattagami Lake Exploration Ltd. Assessment Report.
- Biczok, J., and Kemp, R., 1980, Exploration report no. 3, MARN 1-108 claims, Mattagami Lake Exploration Ltd.,
- Boyle, R.W., 1979, The geochemistry of gold and its deposits: Geol. Surv. Canada Bull. 280.
- Burt, D.M., 1971, Some phase equilibria in the system Ca-Fe-Si-C-O: Carnegie Inst. Washington Year Book 70, p. 178-185.
- , 1972, The facies of some Ca-Fe-Si skarns in Japan: 24th Int. Geol. Congr. (Montreal). Sec. 2, p. 284-288.
- , 1974, Metasomatic zoning in Ca-Fe-Si exoskarns: Carnegie Inst. Washington Pub. 634, p. 243-259.
- Dick, L.A., and Hodgson, C.J., 1982, The MacTung W-Cu (Zn) contact metasomatic and

related deposits of the Northeast Canadian Cordillera: *Econ. Geol.*, v. 77, p. 845-867.

Einaudi, M.T., 1977, Petrogenesis of the copper-bearing skarn at the Mason Valley Mine, Yerington District, Nevada: *Econ. Geol.*, v. 72, p. 769-795

Einaudi, M.T., Meinert, L.D., and Newberry, R.J., 1981, Skarn Deposits: *Econ. Geol.*, 75th Aniv. vol. p. 317-391.

Eugster, H.P., and Ilton, E.S., 1983, Mg-Fe fractionation in metamorphic environments: *in* Saxena, S.K., ed. *Kinetics and equilibrium in metamorphic environments*: p. 115-140.

Ferry, J.M., and Spear, F.S., 1978, Experimental calibration of the partitioning of Fe and Mg between biotite and garnet: *Contrib. Mineralogy Petrology*, v. 66, p. 113-117.

Fletcher, R.C., and Hofmann, A.W., 1974, Simple models of diffusion and combined diffusion-infiltration metasomatism: *Carnegie Inst. Washington, Pub. 634*, p. 243-259

Gordon, T.M., and Greenwood, H.J., 1971, The stability of grossularite in H_2O-CO_2 mixtures: *Am. Mineral.* v. 56, p. 1674-1688.

Hawkins, D.T., and Hultgren, R., 1973, Constitution of binary alloys: *in* *Metals Handbook*, v. 8, Am. Soc. Metals. p. 251-276.

Holdaway, M.J., and Lee, S.M., 1977, Fe-Mg cordierite stability in high-grade pelitic rocks based on experimental, theoretical and natural observations: *Contrib. Mineralogy Petrology*, v. 63, p. 175-198.

Kerrick, D.M., 1977, The genesis of zoned skarns in the Sierra Nevada, California: *Jour. Petrol.*, v. 18, pt 1, p. 144-181.

Korzhinskii, D.S., 1970, Theory of metasomatic zoning: New York, Oxford Clarendon Press. 162p.

Kräuskopf, K.B., 1979, Introduction to geochemistry: McGraw-Hill.

Lambert, M.B., 1966, Geology of the Mount Brenner Stock near Dawson City, Yukon Territory: unpub. M.S thesis, Univ. British Columbia.

Mann, A.W., 1984, Mobility of gold and silver in lateritic weathering profiles: Some observations from Western Australia: Econ. Geol., v 79, p. 38-49.

Meinert, L.D., 1984, Mineralogy and petrology of iron skarns in Western British Columbia, Canada: Econ. Geol., v. 79, p. 869-882.

Nokleberg, W.J., 1981, Geologic setting, petrology, and geochemistry of zoned tungsten-bearing skarns at the Strawberry Mine, Central Sierra Nevada, California: Econ. Geol., v. 76, p. 111-133.

Ohmoto, H., and Kerrick, D., 1970, Devolatilization equilibria in graphitic systems: Am. J. Sci., v. 277, p. 1013-1044.

Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1979, Thermodynamic properties of minerals and related substances at 298.15K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperature: U.S. Geol. Surv. Bull. 1452.

Sato, K., 1980, Tungsten skarn deposit of Fujigatani Mine, southwest Japan: Econ. Geol., v. 75, p. 1066-1082.

Seward, T.M., 1973, Thio complexes of gold and the transport of gold in hydrothermal ore solutions: Geochim. Cosmochim. Acta, v. 37, no. 3, p. 379-399.

- Shimazaki, H., 1980, Characteristics of skarn deposits and related acid magmatism in Japan: *Econ. Geol.*, v. 75, p. 173-183.
- Shoji, T., 1980, The stability of clinopyroxene of the diopside-hedenbergite series in H_2O-CO_2 mixtures: *J. Japan. Assoc. Min. Petr. Econ. Geol.*, v. 75, p. 221-229.
- Smith, D.G.W., and Gold, C.M., 1979, EDATA2: a FORTRANIV program for processing wavelength and / or energy-dispersive electron-microprobe data: *Proc. 14th Ann. Conf. Microbeam Anal. Soc.*, San Antonio, Texas. p. 273-278.
- Taylor, B.E., and O'Neil, J.R., 1977, Stable isotope studies of metasomatic Ca-Fe-Al-Si skarns and associated metasomatic and igneous rocks, Osgood Mountains, Nevada: *Contr. Mineralogy Petrology*, v. 63, p. 1-49.
- Tempelman-Kluit, D.J., 1970, Stratigraphy and structure of the "Keno Hill Quartzite" in Tombstone River-Upper Klondike River Map Areas, Yukon Territory. (166B/7, B18): *Geol. Surv. Canada, Bull. no. 180*.
- Thompson, R.I., and Roots, C.F., Ogilvie Mountains Project, Yukon; Part A: A new regional mapping program: Current research, part A, *Geol. Surv. Canada, Pap. 82-1A*, p. 403-411.
- Uytenbogaardt, W., and Burke, E.A.G., 1971, *Tables for microscopic identification of ore minerals*: Elsevier, 2nd ed.
- Winkler, H.G.F., 1979, *Petrogenesis of metamorphic rocks*: Springer-Verlag, 5th ed.
- Zharikov, V.A., 1970, Skarns: *Int. Geol. Rev.*, v. 12, no. 5, p. 541-559; no. 6, p. 619-647, 760-775.

APPENDIX 1. COMPLETE ELECTRON MICROPROBE ANALYSES OF SKARN SILICATES

* Rock specimens from exposures.

Sample numbers from drill core indicate DDH-number and the depth in metres, eg 10-66.5.

na not analysed.

nd below detection limit.

The statistical error in the results for each element at the 99% confidence level is approximately +1% for major elements and as high as +10% for minor elements.

Table 1
Pyroxene analyses from the inner zone, Mini-Grid.

Sample no.	10-48.8										10-54									
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
NaO	0.309	0.354	0.179	0.116	bd	0.364	0.143	0.230	0.185	0.245	0.309	0.354	0.179	0.116	bd	0.364	0.143	0.230	0.185	0.245
MgO	6.645	7.256	5.739	9.436	8.958	4.130	6.198	6.339	2.701	2.815	6.645	7.256	5.739	9.436	8.958	4.130	6.198	6.339	2.701	2.815
Al ₂ O ₃	1.081	1.085	0.941	1.207	1.438	0.605	0.169	0.237	0.363	0.347	1.081	1.085	0.941	1.207	1.438	0.605	0.169	0.237	0.363	0.347
SiO ₂	50.647	50.725	50.664	51.679	51.579	50.414	50.742	50.870	49.758	49.898	50.647	50.725	50.664	51.679	51.579	50.414	50.742	50.870	49.758	49.898
CaO	23.367	23.441	23.231	23.539	23.317	23.041	22.503	22.852	22.925	22.524	23.367	23.441	23.231	23.539	23.317	23.041	22.503	22.852	22.925	22.524
FeO	18.175	16.916	19.534	13.844	14.792	22.076	19.902	18.967	24.216	23.989	18.175	16.916	19.534	13.844	14.792	22.076	19.902	18.967	24.216	23.989
TiO ₂	bd	bd	bd	bd	0.104	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.104	bd	bd	bd	bd	bd
V ₂ O ₅	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Cr ₂ O ₃	bd	bd	bd	bd	0.145	bd	bd	bd	0.135	0.141	bd	bd	bd	bd	0.145	bd	bd	bd	0.135	0.141
MnO	0.212	0.175	0.186	0.229	0.217	0.242	0.417	0.310	0.245	0.372	0.212	0.175	0.186	0.229	0.217	0.242	0.417	0.310	0.245	0.372
TOTAL%	100.436	99.952	100.478	100.042	100.550	100.872	100.074	99.805	100.819	100.331	100.436	99.952	100.478	100.042	100.550	100.872	100.074	99.805	100.819	100.331
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS																				
Na	0.0233	0.0268	0.0136	0.0086	0.0000	0.0279	0.0110	0.0175	0.0144	0.0190	0.0233	0.0268	0.0136	0.0086	0.0000	0.0279	0.0110	0.0175	0.0144	0.0190
Mg	0.3863	0.4215	0.3352	0.5382	0.5105	0.2434	0.3640	0.3719	0.1611	0.1682	0.3863	0.4215	0.3352	0.5382	0.5105	0.2434	0.3640	0.3719	0.1611	0.1682
Al	0.0497	0.0498	0.0435	0.0544	0.0648	0.0282	0.0078	0.0110	0.0171	0.0104	0.0497	0.0498	0.0435	0.0544	0.0648	0.0282	0.0078	0.0110	0.0171	0.0104
Si	1.9755	1.9771	1.9853	1.9777	1.9721	1.9931	1.9994	2.0022	1.9911	1.9997	1.9755	1.9771	1.9853	1.9777	1.9721	1.9931	1.9994	2.0022	1.9911	1.9997
Ca	0.9765	0.9789	0.9757	0.9648	0.9552	0.9760	0.9500	0.9637	0.9829	0.9671	0.9765	0.9789	0.9757	0.9648	0.9552	0.9760	0.9500	0.9637	0.9829	0.9671
Fe ²⁺	0.5929	0.5514	0.6402	0.4431	0.4780	0.7299	0.6558	0.6243	0.8104	0.8040	0.5929	0.5514	0.6402	0.4431	0.4780	0.7299	0.6558	0.6243	0.8104	0.8040
Ti	0.0000	0.0000	0.0000	0.0025	0.0030	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0025	0.0030	0.0000	0.0000	0.0000	0.0000	0.0000
V	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0036	0.0037	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0036	0.0037
Cr	0.0000	0.0000	0.0000	0.0000	0.0044	0.0000	0.0000	0.0000	0.0078	0.0118	0.0000	0.0000	0.0000	0.0000	0.0044	0.0000	0.0000	0.0000	0.0078	0.0118
Mn	0.0070	0.0058	0.0062	0.0074	0.0070	0.0081	0.0139	0.0103	0.0099	0.0000	0.0070	0.0058	0.0062	0.0074	0.0070	0.0081	0.0139	0.0103	0.0099	0.0000
Hd	0.6012	0.5632	0.6522	0.4482	0.4774	0.7437	0.6344	0.6203	0.8258	0.8270	0.6012	0.5632	0.6522	0.4482	0.4774	0.7437	0.6344	0.6203	0.8258	0.8270
Di	0.3917	0.4307	0.3415	0.5444	0.5154	0.2480	0.3521	0.3695	0.1642	0.1730	0.3917	0.4307	0.3415	0.5444	0.5154	0.2480	0.3521	0.3695	0.1642	0.1730
Jo	0.0070	0.0060	0.0060	0.0070	0.0070	0.0080	0.0134	0.0102	0.0101	0.0000	0.0070	0.0060	0.0060	0.0070	0.0070	0.0080	0.0134	0.0102	0.0101	0.0000

Table 1 cont.

Sample no.	20-63.34	29-92.1	21-43.6				24-29.2			
Analysis no.	P21	P22	P23	P24	P25	P26	P27	P28	P29	P30
NaO	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
MgO	11.040	5.196	4.944	3.365	3.358	4.530	8.126	8.142	8.561	5.902
Al ₂ O ₃	0.307	bd	bd	bd	0.149	bd	6.570	6.420	6.153	0.479
SiO ₂	52.302	50.559	50.504	50.083	50.172	50.454	46.765	47.114	47.628	50.831
CaO	24.133	22.870	22.872	22.543	22.754	22.897	24.129	23.969	24.249	23.465
FeO	11.357	19.959	20.640	22.682	22.626	21.229	13.755	13.304	12.827	18.318
TiO ₂	bd	bd	bd	bd	bd	bd	0.198	0.230	0.217	bd
V ₂ O ₅	0.269	0.164	0.224	0.175	0.172	0.152	0.460	0.509	0.501	0.128
Cr ₂ O ₃	0.371	0.299	0.282	0.233	0.232	0.201	0.685	0.637	0.599	0.214
Mn	bd	0.438	0.515	0.590	0.711	0.442	bd	bd	bd	0.248
TOTAL%	99.778	99.485	99.981	99.671	100.174	99.905	100.688	100.325	100.735	99.585
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS										
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mg	0.6255	0.3076	0.2922	0.2015	0.2001	0.2686	0.4644	0.4654	0.4862	0.3463
Al	0.0138	0.0000	0.0000	0.0000	0.0000	0.0000	0.2969	0.2901	0.2763	0.0222
Si	1.9881	2.0082	2.0030	2.0117	2.0058	2.0073	1.7931	1.8067	1.8147	2.0006
Ca	0.9829	0.9733	0.9719	0.9702	0.9747	0.9760	0.9912	0.9948	0.9899	0.9895
Fe ²⁺	0.3610	0.6630	0.6846	0.7619	0.7565	0.7063	0.4410	0.4267	0.4087	0.6029
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0057	0.0066	0.0062	0.0000
V	0.0068	0.0043	0.0059	0.0046	0.0045	0.0040	0.0117	0.0129	0.0126	0.0033
Cr	0.0111	0.0094	0.0088	0.0074	0.0073	0.0063	0.0208	0.0193	0.0180	0.0067
Mn	0.0000	0.0147	0.0173	0.0201	0.0241	0.0149	0.0000	0.0000	0.0000	0.0083
Hd	0.3659	0.6729	0.6887	0.7747	0.7714	0.7202	0.4871	0.4713	0.4567	0.6297
Di	0.6341	0.3122	0.2939	0.2049	0.2040	0.2739	0.5129	0.5140	0.5433	0.3617
Jo	0.0000	0.0149	0.0174	0.0204	0.0246	0.0152	0.0000	0.0000	0.0000	0.0087

Table 1. cont.

Sample no.	24-29.2	24-12.5	35-91.1	28-8						
Analysis no.	P31	P32	P33	p34	P35	P36	P37	P38	P39	P40
NaO	bd	bd	bd	bd	bd	bd	bd	0.525	0.488	0.543
MgO	6.493	6.254	12.154	13.246	13.651	14.019	7.213	6.443	6.042	0.543
Al ₂ O ₃	1.054	0.716	bd	0.182	bd	bd	bd	0.602	0.865	0.633
SiO ₂	50.519	50.852	52.813	52.862	53.218	53.544	51.826	50.747	50.527	50.511
CaO	23.320	23.375	24.580	24.503	24.686	24.399	23.577	23.291	23.082	23.142
FeO	17.327	17.800	9.388	7.772	7.111	6.507	17.595	17.661	18.228	18.824
TiO ₂	0.191	0.089	bd	0.186	bd	0.110	bd	bd	0.302	bd
V ₂ O ₅	0.192	0.155	0.240	0.295	0.196	0.240	0.234	0.370	0.365	0.396
Cr ₂ O ₃	0.245	0.328	0.370	0.419	0.372	0.367	0.373	0.575	0.545	0.678
MnO ₂	0.348	0.304	0.098	bd	bd	bd	0.540	0.106	0.132	0.091
TOTAL%	99.689	99.874	99.643	99.465	99.234	99.186	101.358	100.320	100.576	100.278

		NUMBER OF IONS ON THE BASIS OF 6 OXYGENS									
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0397	0.0339	0.0413	
Mg	0.3789	0.3649	0.6843	0.7413	0.7633	0.7808	0.4144	0.3747	0.3513	0.3913	
Al	0.0222	0.0330	0.0000	0.0081	0.0000	0.0000	0.0000	0.0277	0.0398	0.0293	
Si	1.9779	1.9908	1.9948	1.9847	1.9963	2.0008	1.9975	1.9799	1.9709	1.9824	
Ca	0.9782	0.9805	0.9947	0.9856	0.9922	0.9768	0.9736	0.9736	0.9647	0.9731	
Fe ⁺⁺	0.5673	0.5828	0.2965	0.2440	0.2231	0.2034	0.5671	0.5762	0.5946	0.6179	
Ti	0.0056	0.0026	0.0000	0.0052	0.0000	0.0031	0.0000	0.0089	0.0000	0.0000	
V	0.0050	0.0040	0.0060	0.0073	0.0048	0.0059	0.0060	0.0095	0.0094	0.0103	
Cr	0.0076	0.0101	0.0111	0.0124	0.0110	0.0108	0.0114	0.0177	0.0168	0.0210	
Mn	0.0115	0.0101	0.0031	0.0000	0.0000	0.0000	0.0179	0.0035	0.0044	0.0030	
Hd	0.5924	0.6085	0.3012	0.2277	0.2262	0.2067	0.5674	0.6037	0.6257	0.6572	
Di	0.3956	0.3810	0.6955	0.7523	0.7738	0.7933	0.4146	0.3926	0.3697	0.3396	
Jo	0.0120	0.0105	0.0002	0.0000	0.0000	0.0000	0.0180	0.0037	0.0046	0.0032	

Table 1. cont.

Sample no.	28-8			P43
	Analysis	P41	P42	
no.				
NaO	0.494	0.380	0.273	
MgO	4.830	5.655	4.389	
Al ₂ O ₃	0.502	0.576	bd	
SiO ₂	50.246	50.374	50.687	
CaO	23.016	22.957	23.510	
FeO	20.128	18.902	20.938	
TiO ₂	bd	bd	bd	
V ₂ O ₅	0.383	0.497	0.328	
Cr ₂ O ₃	0.585	0.768	0.613	
MnO ₂	0.134	0.170	0.215	
TOTAL%	100.318	100.279	100.953	
				NUMBER OF IONS ON THE BASIS OF 6 OXYGENS
Na	0.0378	0.0289	0.0208	
Mg	0.2842	0.3309	0.2576	
Al	0.0234	0.0267	0.0000	
Si	1.9835	1.9774	1.9964	
Ca	0.9735	0.9655	0.9921	
Fe ⁺⁺	0.6645	0.6205	0.6897	
Ti	0.0000	0.0000	0.0000	
V	0.0100	0.0129	0.0085	
Cr	0.0183	0.0238	0.0191	
Mn	0.0045	0.0056	0.0072	
Hd	0.6971	0.6484	0.7226	
Di	0.2981	0.3458	0.2699	
Jo	0.0047	0.0058	0.0075	

Table 2. cont.

Sample no.	27-72.1		27-70.45		27-66.4				4-1*	
	P64	P65	P66	P67	P68	P69	P70	P71	P72	
Analysis no.										
NaO	bd	bd	bd	bd	bd	bd	bd	0.262	0.353	
MgO	3.328	3.052	7.475	9.659	9.711	9.332	2.188	8.255	10.738	
Al ₂ O ₃	0.459	bd	1.344	0.570	0.228	0.228	bd	bd	0.455	
SiO ₂	50.158	49.697	50.020	51.574	51.798	52.019	49.921	51.814	52.660	
CaO	23.246	23.005	23.114	23.947	24.085	24.194	23.286	24.032	24.460	
FeO	22.714	22.497	14.460	12.808	13.142	13.585	22.999	14.714	10.852	
TiO ₂	bd	bd	bd	bd	bd	bd	bd	bd	bd	
V ₂ O ₅	0.295	0.115	0.816	0.341	0.277	0.186	0.447	0.437	0.774	
Cr ₂ O ₃	0.379	0.413	1.917	0.735	0.383	0.353	na	0.945	1.004	
Mn	bd	0.279	bd	bd	bd	bd	0.617	bd	bd	
TOTAL%	100.579	99.058	99.146	99.634	99.624	99.897	99.458	100.459	101.296	
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS										
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0195	0.0256	
Mg	0.1972	0.1840	0.4340	0.5525	0.5560	0.5537	0.1317	0.4730	0.5993	
Al	0.0215	0.0000	0.0617	0.0258	0.0103	0.0103	0.0000	0.0000	0.0201	
Si	1.9940	2.0103	1.9483	1.9790	1.9899	1.9961	2.0156	1.9917	1.9719	
Ca	0.9901	0.9971	0.9646	0.9845	0.9913	0.9947	1.0073	0.9898	0.9814	
Fe ²⁺	0.7551	0.7611	0.4710	0.4110	0.4222	0.4360	0.7766	0.4730	0.3398	
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
V	0.0077	0.0031	0.0210	0.0086	0.0070	0.0047	0.0127	0.0111	0.0192	
Cr	0.0119	0.0133	0.0590	0.0223	0.0116	0.0107	-	0.0287	0.0297	
Mn	0.0000	0.0096	0.0000	0.0000	0.0000	0.0000	0.0211	0.0000	0.0000	
Hd	0.7929	0.7972	0.5204	0.4266	0.4316	0.4496	0.8356	0.5000	0.3618	
Di	0.2071	0.1927	0.4796	0.5744	0.5684	0.5504	0.1417	0.5000	0.6382	
Jo	0.0000	0.0100	0.0000	0.0000	0.0000	0.0000	0.0341	0.0000	0.0000	

Table 3.
Pyroxene analyses from pyroxene-quartz skarn, Mineral Gully.

Sample no.	1-120A	15-37.2	8-8-5*									
Analysis no.	P73	P74	P75	P76	P77	P78	P79	P80	P81	P82		
NaO	bd	0.534	bd	0.303	0.312	0.422	0.416	0.267	0.546	0.493		
MgO	2.315	1.793	2.449	2.281	1.814	1.872	1.770	0.762	5.093	2.765		
Al ₂ O ₃	0.166	0.152	0.800	bd	0.179	bd	bd	bd	0.230	bd		
SiO ₂	49.130	49.335	49.281	49.480	49.503	49.287	49.131	49.641	50.664	49.805		
CaO	22.109	22.261	22.289	22.448	22.391	22.386	22.375	22.505	22.953	22.371		
FeO	24.735	24.064	23.594	23.626	24.633	23.894	24.265	25.817	19.486	22.646		
TiO ₂	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd		
V ₂ O ₅	0.142	0.288	0.420	0.313	0.405	0.340	0.377	0.411	0.412	0.291		
Cr ₂ O ₃	0.239	0.543	0.728	0.624	0.591	0.546	0.531	0.719	0.605	0.580		
MnO	0.629	0.674	0.734	0.681	0.653	0.723	0.622	1.147	0.522	0.528		
TOTAL%	99.465	99.644	100.295	99.756	100.481	99.470	99.487	101.269	100.511	99.479		
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS												
Na	0.0000	0.0420	0.0000	0.0238	0.0244	0.0333	0.0328	0.0209	0.0416	0.0386		
Mg	0.1404	0.1085	0.1466	0.1375	0.1090	0.1135	0.1074	0.0457	0.2985	0.1663		
Al	0.0079	0.0073	0.0379	0.0000	0.0085	0.0000	0.0000	0.0000	0.0107	0.0000		
Si	1.9994	2.0028	1.9789	2.0019	1.9955	2.0040	2.0006	2.0005	1.9922	2.0091		
Ca	0.9640	0.9683	0.9589	0.9731	0.9670	0.9752	0.9762	0.9717	0.9670	0.9669		
Fe ⁺⁺	0.8419	0.8170	0.7923	0.7994	0.8304	0.8125	0.8263	0.8701	0.6408	0.7604		
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		
V	0.0038	0.0077	0.0111	0.0084	0.0108	0.0091	0.0101	0.0110	0.0107	0.0077		
Cr	0.0077	0.0174	0.0231	0.0200	0.0177	0.0175	0.0171	0.0229	0.0188	0.0185		
Mn	0.0217	0.0232	0.0250	0.0233	0.0223	0.0249	0.0215	0.0392	0.0174	0.0180		
Hd	0.8385	0.8612	0.8220	0.8325	0.8635	0.8545	0.8651	0.9111	0.6688	0.8056		
Di	0.1398	0.1144	0.1521	0.1432	0.1133	0.1194	0.1124	0.0479	0.3120	0.1754		
Jo	0.0216	0.0245	0.0259	0.0247	0.0232	0.0262	0.0225	0.0410	0.0182	0.0190		

Table 3, cont.

Sample no.	29-8*	8-8-4*	15-25.2			
Analysis no.	P93	P94	P95	P96	P97	
NaO	bd	na	na	na	na	
MgO	12.984	0.540	2.343	0.800	0.266	
Al ₂ O ₃	0.223	0.566	0.253	0.386	bd	
SiO ₂	53.582	48.688	49.469	48.905	49.040	
CaO	25.054	22.220	22.812	22.606	22.561	
FeO	8.169	27.705	23.793	26.401	25.990	
TiO ₂	0.209	bd	bd	bd	bd	
V ₂ O ₅	0.309	bd	0.335	0.336	0.307	
Cr ₂ O ₃	0.399	0.104	0.606	0.560	0.555	
MnO ₂	bd	0.529	0.678	0.655	1.738	
TOTAL%	100.929	100.352	100.289	100.649	100.457	
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS						
Na	0.0000	0.0329	0.1406	0.0484	0.0162	
Mg	0.7173	0.0273	0.0120	0.0185	0.0000	
Al	0.0097	1.9909	1.9912	1.9858	2.0013	
Si	1.9795	0.9735	0.9838	0.9835	0.9865	
Ca	0.9946	0.9474	0.8009	0.8965	0.8870	
Fe ⁺⁺	0.2532	0.0000	0.0000	0.0000	0.0000	
Ti	0.0000	0.0000	0.0089	0.0090	0.0083	
V	0.0076	0.0183	0.0193	0.0180	0.0179	
Cr	0.0117	0.0183	0.0231	0.0225	0.0601	
Mn	0.0000	0.0183	0.0231	0.0225	0.0601	
Hd	0.2610	0.9487	0.8303	0.9267	0.9208	
Di	0.7390	0.0329	0.1458	0.0500	0.0168	
Jo	0.0000	0.0183	0.0239	0.0233	0.0624	

Table 4.
Pyroxenes analyses from the andradite-bearing skarn, Mineral Gully.

Analysis no.	P98	P99	P100	P101	P102	P103	P104	P105
NaO	bd	0.339	0.333	bd	bd	bd	bd	bd
MgO	5.739	1.750	1.580	17.323	12.646	2.917	bd	bd
Al ₂ O ₃	bd	bd	bd	bd	bd	bd	bd	bd
SiO ₂	49.615	49.789	49.553	55.381	53.667	49.835	48.652	48.726
CaO	23.102	22.874	22.758	25.837	24.671	22.951	22.260	22.134
FeO	19.650	24.854	25.214	2.082	9.553	23.743	28.337	28.655
TiO ₂	bd	bd	bd	0.118	bd	bd	bd	bd
V ₂ O ₅	0.132	0.311	0.319	0.331	0.290	0.139	bd	bd
CrO ₃	0.271	0.488	0.521	0.430	0.396	0.319	0.260	0.202
MnO ₂	0.357	0.413	0.436	bd	0.222	0.496	0.640	0.427
TOTAL%	98.866	100.818	100.714	101.502	101.445	100.400	100.149	100.144
NUMBER OF IONS ON THE BASIS OF 6 OXYGENS								
Na	0.0000	0.0264	0.0260	0.0000	0.0000	0.0000	0.0000	0.0000
Mg	0.3426	0.1048	0.0950	0.9263	0.6992	0.1745	0.0000	0.0000
Al	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Si	1.9870	2.0015	1.9985	1.9868	1.9908	2.0001	2.0034	2.0061
Ca	0.9913	0.9852	0.9834	0.9931	0.9805	0.9869	0.9821	0.9764
Fe	0.6581	0.8356	0.8504	0.0625	0.2964	0.7969	0.9759	0.9866
Ti	0.0000	0.0000	0.0000	0.0032	0.0000	0.0000	0.0000	0.0000
V	0.0035	0.0083	0.0085	0.0078	0.0071	0.0037	0.0000	0.0000
Cr	0.0086	0.0155	0.0166	0.0122	0.0116	0.0101	0.0085	0.0068
Mn	0.0121	0.0140	0.0149	0.0000	0.0070	0.0169	0.0223	0.0149
Hd	0.6498	0.8755	0.8856	0.0633	0.2956	0.8063	0.9777	0.9851
Di	0.3383	0.1098	0.0989	0.9367	0.6974	0.1766	0.0000	0.0000
Jo	0.0119	0.0147	0.0155	0.0000	0.0700	0.0171	0.0223	0.0149

Table 5.
Pyroxene analyses from wollastonite-anorthite skarn and wollastonite marble.

Sample no.	Analysis no.	3-11*					
		JJ2*	P106	P107	P108	P109	P110 P111 P112
NaO	bd	bd	bd	bd	bd	bd	bd
MgO	9.450	8.955	8.160	8.542	9.115	12.292	12.354
Al ₂ O ₃	1.089	2.739	6.682	6.819	5.192	0.651	0.160
SiO ₂	51.022	49.838	46.307	46.176	47.999	53.379	53.618
CaO	24.121	24.107	24.078	23.959	24.142	24.116	24.639
FeO	12.651	13.064	11.986	11.542	11.656	7.709	8.545
TiO ₂	0.177	0.486	1.402	1.317	1.084	0.134	0.118
V ₂ O ₅	0.198	0.194	0.221	0.129	0.196	0.630	0.379
CrO ₃	0.259	0.333	0.310	0.264	0.383	1.066	0.526
MnO	0.377	0.370	0.343	0.234	0.377	bd	bd
TOTAL%	99.344	100.086	99.489	98.982	100.144	99.977	100.339

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS											
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mg	0.5428	0.5121	0.4692	0.4923	0.5189	0.6827	0.6866	0.6827	0.6866	0.6827	0.6866
Al	0.0495	0.1239	0.3038	0.3108	0.2337	0.0286	0.0070	0.0286	0.0070	0.0286	0.0070
Si	1.9661	1.9121	1.7863	1.7855	1.8331	1.9890	1.9993	1.9890	1.9993	1.9890	1.9993
Ca	0.9959	0.9910	0.9951	0.9926	0.9878	0.9628	0.9824	0.9628	0.9824	0.9628	0.9824
Fe ⁺⁺	0.4077	0.4192	0.3867	0.3732	0.3723	0.2402	0.2665	0.2402	0.2665	0.2402	0.2665
Ti	0.0051	0.0140	0.0407	0.0383	0.0311	0.0038	0.0033	0.0038	0.0033	0.0038	0.0033
V	0.0050	0.0049	0.0056	0.0033	0.0049	0.0155	0.0093	0.0155	0.0093	0.0155	0.0093
Cr	0.0079	0.0101	0.0095	0.0081	0.0116	0.0314	0.0155	0.0314	0.0155	0.0314	0.0155
Mn	0.0123	0.0120	0.0112	0.0077	0.0122	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Hd	0.4235	0.4444	0.4460	0.4274	0.4121	0.2603	0.2796	0.2603	0.2796	0.2603	0.2796
Di	0.5638	0.5429	0.5411	0.5638	0.5744	0.7397	0.7204	0.7397	0.7204	0.7397	0.7204
Jo	0.0128	0.0127	0.0129	0.0088	0.0135	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 6. cont.

Sample no.	37-215.5
Analysis no.	P123
NaO	bd
MgO	3.562
Al ₂ O ₃	bd
SiO ₂	49.731
CaO	23.448
FeO	21.282
TiO ₂	bd
V ₂ O ₅	0.348
Cr ₂ O ₃	0.634
MnO ₂	0.685
TOTAL%	99.690

Na	0.0000
Mg	0.2129
Al	0.0000
Si	1.9945
Ca	1.0076
Fe ²⁺	0.7138
Ti	0.0000
V	0.0092
Cr	0.0201
Mn	0.0233
Hd	0.7514
Di	0.2241
Jo	0.0245

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

Table 7.
Analyses of igneous pyroxenes.

Analysis no.	P124	P125	P126	P127	P128	P129	P130	P131	P132
NaO	bd	bd	0.146	bd	bd	bd	0.420	0.664	0.510
MgO	12.297	12.031	11.705	12.242	12.178	12.057	8.387	8.415	8.490
Al ₂ O ₃	2.043	0.968	1.321	0.961	1.321	0.650	0.804	1.708	2.184
SiO ₂	51.458	52.219	51.062	51.778	52.289	51.650	50.874	50.250	49.419
CaO	20.193	21.162	20.172	20.911	20.703	20.360	21.856	21.147	20.146
FeO	12.424	12.459	13.490	12.225	11.849	13.285	16.532	16.726	17.121
TiO ₂	0.642	0.199	0.260	0.098	0.292	0.230	0.209	0.281	0.204
V ₂ O ₅	0.227	0.178	0.152	0.155	0.152	0.225	0.399	0.306	0.299
Cr ₂ O ₃	0.297	0.252	0.224	0.250	0.243	0.259	0.539	0.486	0.386
MnO ₂	0.353	0.498	0.505	0.409	0.438	0.613	0.243	0.332	0.252
TOTAL%	99.934	99.966	99.037	99.029	99.465	99.329	100.263	100.315	99.006

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS									
Na	0.0000	0.0000	0.0109	0.0000	0.0000	0.0000	0.0315	0.0498	0.0388
Mg	0.6922	0.6788	0.6698	0.6965	0.6871	0.6872	0.4834	0.4851	0.4956
Al	0.0909	0.0432	0.0598	0.0432	0.0589	0.0293	0.0367	0.0779	0.1008
Si	1.9433	1.9769	1.9604	1.9765	1.9793	1.9752	1.9675	1.9434	1.9350
Ca	0.8170	0.8583	0.8298	0.8553	0.8396	0.8342	0.9057	0.8763	0.8453
Fe ²⁺	0.3924	0.3944	0.4331	0.3903	0.3751	0.4249	0.5347	0.5410	0.5607
Ti	0.0182	0.0057	0.0075	0.0028	0.0083	0.0066	0.0061	0.0082	0.0060
V	0.0057	0.0044	0.0039	0.0039	0.0038	0.0057	0.0165	0.0078	0.0077
Cr	0.0089	0.0075	0.0068	0.0075	0.0073	0.0078	0.0086	0.0149	0.0120
Mn	0.0113	0.0160	0.0164	0.0132	0.0141	0.0199	0.0102	0.0109	0.0084

Table 8.
Amphibole analyses.

Sample no.	10-48.8	10-54	10-54.5							10-57.0		10-58.5	
Analysis no.	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10			
H ₂ O	1.359	1.566	1.088	2.430	2.115	1.165	1.345	1.654	1.316	1.380			
Na ₂ O	1.083	0.194	0.143	0.413	0.957	0.647	0.699	0.395	0.603	0.475			
MgO	4.935	7.682	7.698	7.200	4.584	5.350	5.750	6.263	5.325	5.967			
Al ₂ O ₃	6.314	0.348	0.565	1.478	4.774	2.319	3.553	1.748	4.215	3.104			
SiO ₂	46.301	52.497	52.632	50.603	46.212	49.596	48.618	50.359	47.721	49.512			
K ₂ O	0.497	bd	bd	0.141	0.561	0.246	0.430	0.193	0.458	0.396			
CaO	11.513	11.235	11.673	11.843	11.682	11.008	11.373	11.483	11.401	11.489			
FeO	27.652	26.030	25.737	25.503	27.973	28.543	26.942	27.491	28.500	27.107			
TiO ₂	0.109	bd	bd	bd	bd	bd	0.166	0.099	0.111	0.097			
V ₂ O ₅	bd	bd	bd	bd	0.235	0.210	0.226	bd	bd	bd			
Cr ₂ O ₃	bd	bd	bd	bd	0.569	0.472	0.601	bd	bd	bd			
MnO ₂	0.239	0.447	0.464	0.389	0.340	0.440	0.297	0.316	0.351	0.381			
NUMBER OF IONS ON THE BASIS OF 23 OXYGENS													
Na	0.3255	0.0571	0.0417	0.1231	0.2917	0.1936	0.2086	0.1180	0.1813	0.1418			
Mg	1.1406	1.7391	1.7328	1.6522	1.0740	1.2309	1.3198	1.4375	1.2315	1.3686			
Al	1.1540	0.0623	0.1006	1.2683	0.8849	0.4218	0.6448	0.3172	0.7708	0.5629			
Si	7.1801	7.9732	7.9482	7.7907	7.2678	7.6557	7.4873	7.7546	7.4049	7.6185			
K	0.0983	0.0000	0.0000	0.0277	0.1124	0.0484	0.0846	0.0379	0.0907	0.0778			
Ca	1.9129	1.8283	1.8850	1.9530	1.9685	1.8206	1.8766	1.8945	1.8954	1.8942			
Fe	3.5861	3.3061	3.2504	3.2837	3.6790	3.6847	3.4699	3.5402	3.6984	3.4883			
Ti	1.2754	0.0000	0.0000	0.0000	0.0000	0.0000	0.0192	0.0115	0.0129	0.0113			
V	0.0000	0.0000	0.0000	0.0000	0.0244	0.0213	0.0230	0.0000	0.0000	0.0000			
Cr	0.0000	0.0000	0.0000	0.0000	0.0707	0.0576	0.0730	0.0000	0.0000	0.0000			
MnO	0.3136	0.0576	0.0593	0.0507	0.0453	0.0580	0.0388	0.0412	0.0462	0.0497			

Table 8. cont.

Sample no.	10-58.5	10-62.42	24-29.2	13-17*	15-43.1	JB*		
Sample no.	A11	A12	A13	A14	A15	A16	A17	A18
H ₂ O	1.164	1.171	2.817	1.929	1.703	1.971	4.014	3.567
Na ₂ O	0.315	bd	bd	1.024	0.745	0.910	0.943	0.130
MgO	6.281	7.578	6.240	0.675	6.578	5.557	1.126	10.405
Al ₂ O ₃	2.121	0.346	0.868	7.842	3.207	4.368	5.300	2.831
SiO ₂	50.359	52.586	51.100	41.036	48.921	47.458	44.181	50.101
K ₂ O	0.280	0.148	0.272	1.425	0.355	0.428	0.824	0.296
CaO	11.385	12.374	11.518	10.987	11.340	11.139	10.668	11.572
FeO	27.494	25.355	26.730	34.682	26.735	27.759	32.342	20.366
TiO ₂	bd	bd	bd	bd	bd	bd	bd	0.137
V ₂ O ₅	bd	bd	bd	bd	bd	bd	bd	0.126
Cr ₂ O ₃	0.089	0.092	bd	bd	bd	bd	0.130	0.237
MnO ₂	0.452	0.349	0.455	0.400	0.416	0.411	0.472	0.231
NUMBER OF IONS ON THE BASIS OF 23 OXYGENS								
Na	0.0938	0.0000	0.0000	0.3261	0.2228	0.2749	0.3008	0.0382
Mg	1.4361	1.7086	1.4426	0.1652	1.5122	1.2909	0.2759	2.3567
Al	0.3835	0.0617	0.1587	1.5181	0.5830	0.8023	1.0270	0.5071
Si	7.7253	7.9548	7.9255	6.7402	7.5449	7.3964	7.2644	7.6133
K	0.0547	0.0287	0.0537	0.2986	0.0698	0.0846	0.1729	0.0574
Ca	1.8713	2.0055	1.9141	1.9335	1.8738	1.8600	1.8793	1.8841
Fe	3.5272	3.2076	3.4671	4.7639	3.4483	3.6181	4.4472	2.5881
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0157
V	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0127
Cr	0.0108	0.0110	0.0000	0.0000	0.0000	0.0000	0.0167	0.0285
Mn	0.0587	0.0448	0.0598	0.0556	0.0543	0.0542	0.0657	0.0297

Table 9.
Analyses of garnets from Mini-Grid.

Sample no.	27-72.7										27-70.45					27-76.5				
Analysis no.	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10										
MgO	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.194										
Al ₂ O ₃	19.019	18.124	14.066	12.198	12.039	18.149	14.066	17.925	15.467	19.307										
SiO ₂	39.269	38.316	37.556	36.737	36.554	37.907	37.556	38.017	27.515	36.516										
CaO	36.589	36.409	34.234	33.675	33.385	36.217	34.234	36.453	35.850	36.516										
FeO	0.809	0.926	1.554	1.626	1.563	0.833	1.554	1.142	1.743	1.334										
Fe ₂ O ₃	3.594	4.118	6.909	7.228	6.950	3.703	6.909	5.078	7.750	3.458										
TiO ₂	0.646	1.216	0.630	0.567	0.549	1.036	0.630	0.673	0.617	0.388										
Cr ₂ O ₃	0.524	0.519	3.312	4.645	5.153	0.544	3.312	0.720	0.540	0.416										
V ₂ O ₅	0.408	0.321	1.312	1.546	1.617	0.304	1.312	0.483	0.384	0.445										
MnO ₂	0.196	0.133	0.303	0.186	0.236	0.085	0.303	bd	bd	0.213										
TOTAL%	101.054	100.082	99.873	98.408	98.046	98.778	99.876	100.491	99.866	101.581										
STRUCTURAL FORMULA ON THE BASIS OF 8 CATIONS																				
O	11.9893	11.9747	11.9922	11.9829	11.9878	11.9659	11.9922	11.9433	11.9267	11.9808										
Mg	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0217										
Al	1.6972	1.6391	1.3039	1.1560	1.1462	1.6596	1.3039	1.6183	1.4207	1.7127										
Si	2.9732	2.9402	2.9539	2.9541	2.9529	2.9411	2.9539	2.9121	2.9239	2.9587										
Ca	2.9682	2.9934	2.8849	2.9012	2.8895	3.0107	2.8849	2.9918	2.9937	2.9447										
Fe	0.2560	0.2972	0.5111	0.5467	0.5281	0.2702	0.5111	0.3659	0.5681	0.2798										
Ti	0.0368	0.0702	0.0373	0.0343	0.0334	0.0605	0.0373	0.0387	0.0362	0.0219										
Cr	0.0313	0.0315	0.2060	0.2953	0.3291	0.0334	0.2060	0.0436	0.0333	0.0248										
V	0.0248	0.0197	0.0828	0.0997	0.1047	0.0189	0.0828	0.0296	0.0240	0.0221										
Mn	0.0126	0.0086	0.0202	0.0127	0.0162	0.0056	0.0202	0.0000	0.0000	0.0136										
Gr	0.8429	0.8228	0.6156	0.5392	0.5293	0.8368	0.6091	0.7818	0.6884	0.7792										
And	0.1184	0.1486	0.2081	0.2303	0.2169	0.1351	0.2081	0.1789	0.2809	0.1789										
Sp/Alm	0.0106	0.0029	0.0316	0.0329	0.0368	0.0019	0.0384	0.0027	0.0021	0.0184										
Uv	0.0157	0.0158	0.1033	0.1477	0.1646	0.0167	0.1030	0.0218	0.0166	0.0124										
Gold	0.0124	0.0099	0.0414	0.0499	0.0524	0.0095	0.0414	0.0148	0.0120	0.0111										

Table 9. cont.

Sample no.	27-76.5
Analysis no.	G11
MgO	0.284
Al ₂ O ₃	17.502
SiO ₂	38.971
CaO	35.592
FeO	2.280
Fe ₂ O ₃	5.913
TiO ₂	0.284
Cr ₂ O ₃	0.307
V ₂ O ₅	0.419
MnO	0.000
TOTAL%	101.552

STRUCTURAL FORMULA ON THE BASIS OF 8 CATIONS

O	11.9727
Mg	0.0321
Al	1.5680
Si	2.9623
Ca	2.8987
Fe	0.4832
Ti	0.0163
Cr	0.0184
V	0.0210
Mn	0.0000
Gr	0.7554
And	0.1910
Sp/Alm	0.0338
Uv	0.0093
Gold	0.0105

Table 10.

Analyses of garnets from Mineral Gully skarn.

Sample no. Analysis	30-5*		27-1*					37-218.8		
	G12	G13	G14	G15	G16	G17	G18	G19	G20	G21
MgO	0.297	0.028	0.018	0.044	bd	bd	0.231	0.228	bd	bd
Al ₂ O ₃	14.356	14.613	12.824	13.559	14.478	12.962	0.150	0.290	18.443	14.159
SiO ₂	37.586	37.960	37.726	37.141	37.999	37.473	36.093	36.127	38.900	37.832
CaO	32.586	32.898	32.501	32.800	32.695	31.376	33.827	33.765	35.865	34.787
FeO	3.879	3.844	4.514	4.283	2.582	3.066	8.337	8.191	1.134	2.239
Fe ₂ O ₃	10.058	9.968	11.704	11.108	11.477	13.628	21.619	21.240	5.042	9.954
TiO ₂	0.545	0.496	0.534	0.410	0.485	0.880	bd	bd	0.214	0.702
Cr ₂ O ₃	0.275	0.181	0.079	0.168	0.363	0.313	0.557	0.503	0.436	0.423
V ₂ O ₅	na	na	na	na	0.240	0.287	0.305	0.315	0.253	0.335
MnO	0.849	0.907	0.904	0.799	0.835	1.128	0.099	bd	0.452	0.637
TOTAL%	100.431	100.895	100.804	100.312	101.254	101.113	101.218	100.659	100.739	101.068

STRUCTURAL FORMULA ON THE BASIS OF 8 CATIONS										
O	11.9500	11.9636	11.9506	11.9207	12.0185	12.0397	11.7051	11.7173	11.9737	11.9488
Mg	0.0347	0.0033	0.0021	0.0052	0.0000	0.0000	0.0284	0.0281	0.0000	0.0000
Al	1.3262	1.3446	1.1912	1.2609	1.3401	1.2067	0.0146	0.0284	1.6577	1.2983
Si	2.9493	2.9635	2.9735	2.9306	2.9640	2.9599	2.9822	2.9974	2.9667	2.9434
Ca	2.7366	2.7518	2.7446	2.7730	2.7324	2.6554	2.9946	2.9974	2.9306	2.8998
Fe	0.8476	0.8366	0.9917	0.9421	0.8421	1.0126	1.9202	1.8944	0.3617	0.7285
Ti	0.0321	0.0291	0.0317	0.0243	0.0284	0.0522	0.0000	0.0000	0.0123	0.0410
Cr	0.0170	0.0112	0.0049	0.0105	0.0224	0.0196	0.0364	0.0330	0.0263	0.0260
V					0.0154	0.0182	0.0167	0.0173	0.0155	0.0209
Mn	0.0564	0.0600	0.0603	0.0534	0.0552	0.0755	0.0069	0.0000	0.0292	0.0420
Gr	0.5836	0.5875	0.6116	0.5347	0.5770	0.4944	0.0100	0.0144	0.7949	0.6079
And	0.3603	0.3243	0.3008	0.3843	0.3149	0.3718	0.9601	0.9601	0.1608	0.3352
Sp/Alm	0.0876	0.0827	0.0851	0.0757	0.0892	0.1149	0.0023	0.0000	0.0233	0.0334
Uv	0.0085	0.0056	0.0025	0.0053	0.0112	0.0098	0.0184	0.0167	0.0132	0.0130
Gold					0.0077	0.0091	0.0084	0.0088	0.0078	0.0105

Table 10. cont.

Sample no.	37-218.8	JJ*				28-8*			
Analysis no.	G22	G23	G24	G25	G26	G27	G28		
MgO	bd	bd	bd	0.111	0.385	0.360	0.786		
Al ₂ O ₃	17.837	17.824	16.748	17.147	17.458	19.932	16.768		
SiO ₂	38.364	38.334	38.079	38.107	38.051	38.945	38.177		
CaO	35.883	35.678	35.509	35.338	33.822	36.989	37.042		
FeO	1.172	1.177	1.366	1.276	2.210	1.013	1.476		
Fe ₂ O ₃	5.208	5.231	6.074	5.672	5.732	2.627	3.828		
TiO ₂	0.846	0.228	0.617	1.103	0.545	bd	bd		
Cr ₂ O ₃	0.431	0.362	0.286	0.447	1.218	1.149	0.904		
V ₂ O ₅	0.344	0.319	0.286	bd	0.952	0.875	0.751		
MnO ₂	0.556	0.523	0.521	0.359	0.583	bd	bd		
TOTAL%	100.641	99.676	99.609	99.560	100.956	101.891	99.732		

STRUCTURAL FORMULA ON THE BASIS OF 8 CATIONS									
O	11.9660	11.9560	11.9581	11.9755	12.0220	11.9661	11.8880		
Mg	0.0000	0.0000	0.0000	0.0127	0.0440	0.0401	0.0900		
Al	1.6100	1.6215	1.5326	1.5600	1.5813	1.7578	1.5183		
Si	2.9383	2.9589	2.9566	2.9417	2.9243	2.9141	2.9332		
Ca	2.9445	2.9506	2.9540	2.9228	2.7850	2.9655	3.0493		
Fe	0.3752	0.2798	0.4436	0.4119	0.4736	0.2113	0.3161		
Ti	0.0487	0.0132	0.0360	0.0640	0.0315	0.0000	0.0000		
Cr	0.0261	0.0221	0.0251	0.0273	0.0740	0.0680	0.0459		
V	0.0211	0.0197	0.0178	0.0222	0.0484	0.0433	0.0381		
Mn	0.0360	0.0342	0.0343	0.0374	0.0379	0.0000	0.0000		
Gr	0.7752	0.7984	0.7433	0.7634	0.7188	0.8446	0.7914		
And	0.1858	0.1641	0.2160	0.1861	0.1483	0.0884	0.1648		
Sp/Alm	0.0185	0.0165	0.0192	0.0257	0.0717	0.0115	0.0000		
Uv	0.0101	0.0111	0.0126	0.0137	0.0370	0.0340	0.0239		
Gold	0.0106	0.0099	0.0089	0.0111	0.0242	0.0215	0.0199		

Table 11.

Analyses of skarn plagioclases.

Sample no.	27-66.4	27-76.5	37-215.5				JJ*			
Analysis no.	F1	F2	F3	F4	F5	F6	F9			
NaO	1.817	bd	bd	5.878	1.470	5.299	bd			
Al ₂ O ₃	33.689	36.417	36.050	29.960	33.397	27.874	35.886			
SiO ₂	48.399	43.625	43.880	58.381	47.464	56.833	44.024			
K ₂ O	0.523	0.228	0.251	0.507	0.167	0.375	0.160			
CaO	16.283	19.819	19.505	8.626	16.513	9.715	19.724			
Fe ₂ O ₃	0.150	bd	0.096	0.178	0.335	0.209	0.287			
BaO	0.303	0.121	0.198	bd	0.192	0.128	bd			
TOTAL%	101.161	100.218	99.980	100.530	99.348	100.433	100.081			
NUMBER OF IONS ON THE BASIS OF 8 OXYGENS										
Na	0.160	0.0000	0.0000	0.5070	0.1314	0.4593	0.0000			
Al	1.8033	1.9841	1.9680	1.4135	1.8139	1.4686	1.9561			
Si	2.1982	2.0166	2.0325	2.5970	2.1874	2.5406	2.0362			
K	0.0303	0.0134	0.0149	0.0288	0.0098	0.0214	0.0095			
Ca	0.7924	0.9816	0.9680	0.4111	0.8153	0.4653	0.9774			
Fe ²⁺	0.0057	0.0000	0.0037	0.0066	0.0129	0.0078	0.0111			
Ba	0.0054	0.0022	0.0036	0.0000	0.0053	0.0022	0.0000			

Table 12.
Biotite analyses

Sample no.	27-27.83	1-20*								
Analysis no.	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
H ₂ O	4.107	2.707	2.403	3.057	2.509	4.791	3.899	5.370	4.270	4.947
NaO	0.564	0.620	0.554	0.735	0.751	0.608	0.723	0.605	0.667	0.658
MgO	3.817	3.408	2.675	3.004	2.539	7.980	7.836	7.961	8.230	8.412
Al ₂ O ₃	21.190	20.608	19.382	19.627	19.630	17.282	17.719	17.396	17.923	17.310
SiO ₂	31.887	33.115	32.978	32.748	32.855	34.682	34.362	34.370	34.262	34.520
K ₂ O	7.918	8.887	8.901	8.226	8.867	9.113	9.192	9.020	9.112	9.005
CaO	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
FeO	28.014	27.655	28.655	28.673	28.458	20.913	21.452	20.923	21.707	21.303
MnO ₂	bd	bd	bd	bd	bd	0.196	0.218	bd	0.169	0.128
TiO ₂	2.503	3.002	4.292	3.796	4.063	4.334	4.483	4.171	3.542	3.604
Cl	bd	bd	0.206	0.172	0.165	0.131	0.149	0.108	0.152	0.146
NUMBER OF IONS ON THE BASIS OF 22 OXYGENS										
Na	0.1722	0.1868	0.1679	0.2238	0.2279	0.1822	0.2156	0.1824	0.1996	0.1979
Mg	0.8959	0.7888	0.6236	0.7028	0.6386	1.8391	1.7963	1.8438	1.8946	1.9455
Al	3.9324	3.7720	3.5726	3.6304	3.6187	3.2494	3.2120	3.1858	3.2627	3.1655
Si	5.0210	5.1430	5.1576	5.1396	5.1390	5.3628	5.2850	5.3561	5.2921	5.3563
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
K	1.5903	1.7606	1.7757	1.6469	1.7691	1.7976	1.8034	1.7880	1.7955	1.7823
Fe ²⁺	3.6889	3.5919	3.7478	3.7634	3.7224	2.7043	2.7593	2.7189	2.8040	2.7644
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0256	0.0284	0.0000	0.0221	0.0168
Ti	0.2964	0.3506	0.5047	0.4480	0.4779	0.5040	0.5186	0.4874	0.4114	0.4205
Cl	0.0000	0.0000	0.0547	0.0458	0.0436	0.0344	0.0388	0.0283	0.0398	0.0384

Table 12. cont.

Sample no.	1-20*		Igneous	
	Analysis no	B11	B12	B13
H ₂ O		5.067	5.851	5.989
Na ₂ O		0.500	0.479	bd
MgO		7.529	7.492	7.630
Al ₂ O ₃		17.655	17.347	14.819
SiO ₂		34.205	33.955	33.417
CaO		bd	bd	bd
K ₂ O		8.049	8.974	8.362
FeO		21.343	21.325	22.041
MnO ₂		0.174	0.198	0.093
TiO ₂		4.372	4.260	7.650
Cl		0.137	0.156	na
NUMBER OF IONS ON THE BASIS OF 22 OXYGENS				
Na		0.1506	0.1456	0.0000
Mg		1.7440	1.7521	1.7901
Al		3.2337	3.2079	2.7493
Si		5.3159	5.3278	5.2603
Ca		0.0000	0.0000	0.0000
K		1.7940	1.7962	1.6791
Fe ²⁺		2.7739	2.7982	2.9016
Mn		0.0229	0.0264	0.0123
Ti		0.5110	0.5026	0.9056
Cl		0.0360	0.0416	-

Table 13.
Analyses of garnets from the Jurassic Schist.

Sample no.	27-27.83	1-20*									
Analysis no.	GT1	GT2	GT3	GT4	GT5	GT6	GT7	GT8	GT9	GT10	
MgO	2.274	2.226	2.109	1.750	2.083	3.207	3.076	2.775	3.155	3.261	
Al ₂ O ₃	20.937	20.817	20.738	20.862	20.741	21.327	21.322	21.197	21.291	21.091	
SiO ₂	36.801	36.725	36.624	36.941	37.062	36.745	36.700	36.564	36.739	36.238	
CaO	0.617	0.510	0.788	0.905	1.031	0.979	0.824	0.944	1.001	0.985	
FeO	37.568	38.084	37.461	38.344	37.952	32.119	31.759	32.217	32.258	31.585	
TiO ₂	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.132	
MnO ₂	bd	bd	bd	0.089	bd	6.573	7.239	7.434	6.929	6.659	
TOTAL%	98.277	98.362	97.720	98.891	98.869	100.950	100.920	101.131	101.373	99.951	
STRUCTURAL FORMULA ON THE BASIS OF 8 CATIONS											
O	12.0566	12.0421	12.0547	12.0506	12.0460	11.9398	11.9420	11.9273	11.9320	11.9344	
Mg	0.2793	0.2737	0.2609	0.2146	0.2549	0.3819	0.3668	0.3311	0.3751	0.3922	
Al	2.0332	2.0240	2.0287	2.0227	2.0067	2.0080	2.0106	1.9999	2.0018	2.0053	
Si	3.0322	3.0298	3.0400	3.0389	3.0424	2.9355	2.9363	2.9270	2.9308	2.9235	
Ca	0.0616	0.0450	0.0700	0.0797	0.0907	0.0838	0.0706	0.0809	0.0855	0.0851	
Fe	2.5887	2.6276	2.6005	2.6379	2.6054	2.1459	2.1250	2.1569	2.1386	2.1310	
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0080	
Mn	0.0000	0.0000	0.0000	0.0062	0.0000	0.4448	0.4906	0.5041	0.4682	0.4550	
Py	0.0931	0.0929	0.0890	0.0730	0.0864	0.1251	0.1201	0.1077	0.1223	0.1280	
Alm	0.8864	0.8912	0.8871	0.8978	0.8829	0.7018	0.6960	0.7020	0.6972	0.6957	
Sp	0.0000	0.0000	0.0000	0.0021	0.0000	0.1456	0.1607	0.1640	0.1526	0.1485	
Gr	0.0205	0.0153	0.0239	0.0271	0.0307	0.0275	0.0212	0.0263	0.0279	0.0278	

**APPENDIX 2. REACTION CONSTANTS CALCULATED BY SUPCRT AND USED IN THE
CONSTRUCTION OF FIGURES 5.4 AND 5.5**

LogK

	500°C	600°C
1. $4\text{Fe}_2\text{O}_3 + \text{O}_2 = 6\text{Fe}_3\text{O}_4$	19.2478	15.3141
2. $\text{Fe}_3\text{O}_4 + 9\text{SiO}_2 + 3\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} = 9\text{CaFeSi}_2\text{O}_7 + 2\text{O}_2$	-45.9220	-37.7269
3. $2\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} + 4\text{SiO}_2 = 2\text{CaSiO}_3 + 4\text{CaFeSi}_2\text{O}_7 + \text{O}_2$	-23.8890	-19.4836
4. $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 = 3\text{Fe}_2\text{SiO}_5 + \text{O}_2$	-23.4492	-19.7178
5. $4\text{CaFeSi}_2\text{O}_7 + 4\text{CaCO}_3 + \text{O}_2 = 2\text{CaSiO}_3 + 2\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} + \text{CO}_2$	32.6249	30.8054
6. $2\text{Fe}_3\text{O}_4 + 18\text{CaCO}_3 + 18\text{CaFeSi}_2\text{O}_7 + 5\text{O}_2 = 12\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} + 2\text{SiO}_2 + 2\text{CO}_2$	162.4700	150.8470
7. $2\text{CaCO}_3 + 4\text{CaFeSi}_2\text{O}_7 + \text{O}_2 = 2\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} + 2\text{SiO}_2 + 2\text{CO}_2$	28.2571	25.1445
8. $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$	2.1839	2.8305
9. $6\text{CaFeSi}_2\text{O}_7 + 6\text{CO}_2 + \text{O}_2 = 2\text{Fe}_3\text{O}_4 + 12\text{SiO}_2 + 6\text{CaCO}_3$	7.0739	0.0217
10. $4\text{Fe}_3\text{O}_4 + 18\text{CaCO}_3 + 18\text{SiO}_2 + \text{O}_2 = 6\text{Ca}_2\text{Fe}_2\text{Si}_2\text{O}_{11} + 18\text{CO}_2$	70.6219	75.3882
11. $2\text{Fe}_3\text{O}_4 + 6\text{CO}_2 = 6\text{FeCO}_3 + \text{O}_2$	-46.4231	-45.4520
12. $\text{C} + \text{O}_2 = \text{CO}_2$	26.7808	23.7197

APPENDIX 3. REACTION CONSTANTS USED IN THE CONSTRUCTION OF FIGURE 5.7

Data for reaction 1 to 7 from Robie et al. 1979.

Data for reactions 8 to 10 from Barton and Skinner, 1979.

LogK		300°C	400°C
1.	$3/2\text{FeS} + \text{O}_2 = 1/3\text{Fe}_3\text{O}_4 + 3/2\text{S}_2$	20.376	18.365
2.	$\text{FeS} + 3/2\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{S}_2$	30.225	28.446
3.	$3/2\text{FeS} + \text{O}_2 = 1/2\text{Fe}_3\text{O}_4 + 3/4\text{S}_2$	27.435	22.959
4.	$\text{FeS} + \text{S}_2 = 2\text{FeS}_2$	9.408	16.1238
5.	$\text{Fe}_2\text{O}_3 + \text{O}_2 = 6\text{Fe}_3\text{O}_4$	30.343	23.776
6.	$\text{Fe} + \text{S}_2 = 2\text{FeS}$	19.171	15.065
7.	$3/2\text{Fe} + \text{O}_2 = 1/2\text{Fe}_3\text{O}_4$	41.811	34.255
8.	$4/3\text{Bi} + \text{S}_2 = 2/3\text{Bi}_2\text{S}_3$	9.031	6.368
9.	$2\text{FeAs}_2 + 2\text{FeS} + \text{S}_2 = 4\text{FeAsS}$	14.508	12.388
10.	$\text{S}_2 + 5\text{CuFeS}_2 = 4\text{FeS}_2 + \text{Cu}_2\text{FeS}_4$	-6.7529	-3.8836
11.	$3\text{S}_2 + 3\text{FeAs}_2 + \text{Fe}_3\text{O}_4 = 6\text{FeAsS} + 2\text{O}_2$		